This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

Transferred to the Lawrence Scientific School.
Chem 7708.96

Harvard College Library

FROM THE BEQUEST OF

GEORGE HAYWARD, M.D.,

OF BOSTON,

(Class of 1809).

8 Dec. 1899.

SCIENCE CENTER LIBRARY

HARVARD COLLEGE

CHEMISTRY

FOR

ENGINEERS AND MANUFACTURERS.

VOL. II.—CHEMISTRY OF MANUFACTURING PROCESSES.

COMPANION VOLUME.

With Illustrations. In Two Vols., Large 8vo. Sold Separately.

CHEMISTRY FOR ENGINEERS AND MANUFACTURERS.

BY

BERTRAM BLOUNT, F.I.C., F.C.S., ASSOC.INST.C.E., Consulting Chemist to the Crown Agents for the Colonies.

AND

A. G. BLOXAM, F.I.C., F.C.S., Consulting Chemist, Head of the Chemistry Department, Goldsmiths' Institute, New Cross.

VOL. I.—CHEMISTRY OF ENGINEERING, BUILDING, AND METALLURGY. *Ready. Price, 10s. 6d.*

GENERAL CONTENTS.—Introduction—Chemistry of the Chief Materials of Construction—Sources of Energy—Chemistry of Steam Raising—Chemistry of Lubrication and Lubricants—Metallurgical Processes used in the Winning and Manufacture of Metals.

"PRACTICAL THROUGHOUT . . . an ADMIRABLE TEXT-BOOK, useful not only to Students, but to ENGINEERS and MANAGERS OF WORKS in PREVENTING WASTE and IMPROVING PROCESSES."—*Scotsman.*

"A book worthy of HIGH RANK . . . its merit is great and uniformly maintained . . . treatment of the subject of GASEOUS FUEL particularly good. . . . WATER GAS and its production clearly worked out. . . . We WARMLY RECOMMEND the work, and look forward with keen interest to the appearance of Vol. II."—*Journal of Gas Lighting.*

"The first part of this volume will be A VALUABLE GUIDE to persons engaged in DESIGNING CHEMICAL WORKS and PLANT, whilst the second Part is A KEY to more special metallurgical studies."—*Chemical News.*

STANDARD SCIENTIFIC TEXT-BOOKS.

WITH NUMEROUS ILLUSTRATIONS.

ASSAYING, by J. J. and C. BERINGER. THIRD EDITION. 10s. 6d.

BLEACHING AND CALICO-PRINTING, by GEO. DUERR. With Patterns. 12s. 6d.

CEMENTS, by G. R. REDGRAVE. 8s. 6d.

DISINFECTANTS, by DR. RIDEAL. 12s. 6d.

DYEING, by MM. KNECHT AND RAWSON. In 3 Vols. With Patterns. 45s.

DYEING AND CLEANING, by GEO. H. HURST. 4s. 6d.

ELECTRO-METALLURGY, by W. G. M'MILLAN. 10s. 6d.

FOODS, ANALYSIS OF, by WYNTER BLYTH. FOURTH EDITION. 21s.

GAS MANUFACTURE, by W. ATKINSON BUTTERFIELD. 9s.

METALLURGY (ELEMENTS OF), by PHILLIPS & BAUERMAN. THIRD EDITION. 36s.

METALLURGY (INTRODUCTION TO), by PROF. W. C. ROBERTS-AUSTEN. THIRD EDITION. 12s. 6d.

METALLURGY (ELEMENTARY), by PROF. HUMBOLDT SEXTON. 6s.

OILS, SOAPS, AND CANDLES, by DR. ALDER WRIGHT. 28s.

PAINTERS' COLOURS AND VARNISHES, by GEO. H. HURST. SECOND EDITION. 12s. 6d.

PETROLEUM, by BOVERTON REDWOOD, assisted by GEO. T. HOLLOWAY. In 2 Vols. 45s.

PHOTOGRAPHY, by A. BROTHERS. 18s.

POISONS, DETECTION OF, by WYNTER BLYTH. THIRD EDITION. 21s.

*****For STANDARD WORKS on all branches of SCIENCE and TECHNOLOGY, see Messrs. GRIFFIN'S SCIENTIFIC and TECHNICAL CATALOGUE at the end of this volume.**

MEDICAL and GENERAL CATALOGUES sent Post-free on application.

LONDON: CHARLES GRIFFIN & CO., LTD.; EXETER STREET, STRAND.

CHEMISTRY

FOR

ENGINEERS AND MANUFACTURERS.

A PRACTICAL TEXT-BOOK.

BY

BERTRAM BLOUNT,
F.I.C., F.C.S., ASSOC.INST.C.E.,
CONSULTING CHEMIST
TO THE CROWN AGENTS
FOR THE COLONIES.

AND

A. G. BLOXAM,
F.I.C., F.C.S.,
CONSULTING CHEMIST, HEAD OF THE
CHEMISTRY DEPARTMENT, GOLDSMITHS'
INSTITUTE, NEW CROSS.

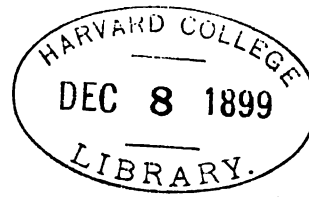
With Illustrations.

VOLUME II.—CHEMISTRY OF MANUFACTURING PROCESSES.

LONDON:
CHARLES GRIFFIN AND COMPANY, LIMITED;
EXETER STREET, STRAND.
1896.

[*All Rights Reserved.*]

Chem 7/108.96



Hayward fund
(II) 260.5

PREFACE.

THE sole object of the chapters comprising this volume is to give the reader a general view of the principles which underlie the several manufactures described. It is in no way intended to present such an account of details as will suffice for the student of any particular industry, as indeed must be obvious from the size of the book.

The usefulness with which the authors venture to accredit their work is to be found in the fact that it seeks to expound those **dominant principles** which are too often hidden beneath masses of mere detail, and are consequently apt to be overlooked by the specialist in any one branch, to his detriment, in that he frequently fails to apply to his own work principles which are matters of common knowledge elsewhere.

These remarks are rendered necessary by the fact that the scope and intention of the first volume of this book appear to have been occasionally misunderstood.

The Bibliography, which will be found at the end of the work, will serve to indicate the sources of information which are at hand for those who desire further details on any particular subject.

In this volume the authors have had the able advice of Mr. Geo. H. Hurst concerning the technique of Bleaching and Dyeing, and they take this opportunity of thanking him for his valuable assistance.

LONDON, *October*, 1896.

CONTENTS.

CHAPTER I.

Sulphuric Acid Manufacture.

	PAGE
Raw Materials for Vitriol Making—	
Sulphur,	1
Pyrites and other Raw Materials,	2
Skeleton of Process of Vitriol Making,	2
Processes and Plant—	
Pyrites Burners,	3
Production of Sulphur Dioxide,	5
Vitriol Chambers,	7
Manufacture of Nitric Acid,	8
Conversion of Sulphur Dioxide into Sulphuric Acid,	11
Concentration,	15
Purification,	16
Nordhausen or Fuming Sulphuric Acid,	17

CHAPTER II.

Manufacture of Alkali and its Bye-Products.

Leblanc Process—	
Raw Materials,	19
Manufacture of Salt Cake,	22
Hydrochloric Acid,	24
Manufacture of Black Ash,	25
Lixiviation of Black Ash,	27
Evaporation of Tank Liquor,	28
Finishing the Soda Ash,	29
Caustic Soda,	30
Commercial Standards for Trading in Alkali,	31
Treatment of Tank Waste,	32
Chlorine and Bleaching Powder—	
Production of Chlorine,	35
Manganese Recovery Process,	37
Deacon's Chlorine Process,	39
Production of Bleaching Powder,	40
Potassium Chlorate,	42
Ammonia-Soda Process—	
Principles and Plant,	43
Production and Recovery of Ammonia,	47
Recovery of Chlorine,	49
Other Chemical Processes for Making Alkali—	
Cryolite Process,	51
Electrolytic Processes,	51
Review of Alkali Manufacture,	53

CHAPTER III.

Destructive Distillation.

General Principles,	55
Destructive Distillation of Coal—	
Kinds of Coal,	56
Carbonising in Retorts for Gas Production,	58
The Process of Distillation,	60
Plant and Purification,	62
Products—Gas,	66
Valuation and Utilisation of Coal Gas,	67

PAGE

Enrichment of Coal Gas, . 71
Oil Gas, ... 74
Gas Liquor, ... 75
Coal Tar, ... 76
Carbonising in Ovens for Coke Production, . . 83
Carbonising Peat, . . 87
Destructive Distillation of Wood—
Burning in heaps or "meilers," . . . 88
Charring in Kilns and Retorts, ... 90
Products—Charcoal, Tar, Wood Spirit, Gas, . 91
Destructive Distillation of Shale—
Retorts, ... 97
Products—Crude Oil or Tar, Ammoniacal Liquor, Gas, ... 100
Destructive Distillation of Bones—
Bone Charcoal, Oil, Ammonia, Gas, . . . 104

CHAPTER IV.

Artificial Manure Manufacture.

Phosphatic Manures—
Mineral Phosphates, Superphosphate, . . . 107
Precipitated Phosphates, Basic Slag, Bones, . 109
Nitrogenous Manures—
Ammonium Sulphate, Nitrate, Organic Nitrogenous Manures, . . 112
Potash Manures, . . . 114
General Manures—
Farmyard Manure, Sewage, Guano, ... 114

CHAPTER V.

Petroleum.

Origin and Distribution, . . 117
Winning of Petroleum, Transmission, ... 118
Refining—
Products of Fractionation, 120
Ozokerite, . . . 123
Asphaltum, . . . 124

CHAPTER VI.

Lime and Cement.

Lime-burning—
Forms of Calcium Carbonate, ... 126
Kilns for Lime-burning, . 128
Cements—
Mortar, Plaster of Paris, . 130
Hydraulic Cements, Hydraulic Lime, . . 132
Roman Cement, Septaria Nodules, . . . 133
Portland Cement, . . 134
Burning and Grinding Cement Clinker, . . 134
Composition and Properties of Portland Cement, . 137
Puzzuolanic Cements, . 140
Artificial Stone, Water Glass, ... 141

CHAPTER VII.

Clay Industries and Glass.

	PAGE
Clay Industries—	
Clays,	143
Bricks and Tiles,	144
Porcelain,	146
Stoneware and Earthenware,	149
Glass—	
Raw Materials,	150
Fusion of Raw Materials to Glass,	152
Annealing and Hardening Glass,	156
Coloured and Opal Glass,	158
Properties of Glass,	160

CHAPTER VIII.

Sugar and Starch.

Sucroses—	
Cane Sugar, Concentration,	162
Beet Sugar, Extraction and Concentration,	165
Utilisation of Uncrystallised Sugar,	172
Osmose Process, Elution Process, Strontia Process,	173
Minor Sources of Sugar,	176
Refining Raw Sugar,	177
Lactose and Maltose,	180
Glucoses—	
Dextrose, Starch Sugar,	181
Lævulose, Invert Sugar,	182
Starch—	
Manufacture of Starch,	184
Wheat Starch, Rice Starch,	185
Maize Starch, Dextrine,	186

CHAPTER IX.

Brewing and Distilling.

Fermentation—	
General Principles,	189
Beer—	
Malt,	190
Malt Adjuncts,	193
Hops and Bitter Principles,	194
Water for Brewing, Yeast,	194
Mashing,	196
Boiling and Cooling,	197
Fermentation of Wort.,	199
Cleansing of the Beer,	203
Racking and Finishing Processes,	204
Wine—	
Grapes,	205
Fermentation of Grape Juice,	206
Fortification of Wines,	207
Minor Fermented Liquors,	208
Spirit—	
Brandy, Whiskey, Gin, Rum,	209
Alcohol, Silent Spirit,	215
Alcoholometry, Methylated Spirit,	218
Vinegar—	
Slow and Quick Vinegar Processes,	219
Factitious Vinegar,	222

CHAPTER X.

Oils, Resins and Varnishes.

	PAGE		PAGE
Fats, Liquid and Solid—		Turpentines, Resins, Caoutchouc—	
Constitution of Fats and Oils, Saponification, .	223	Turpentine, Essential Oils,	240
Classification of the Chief Fats and Oils, . .	226	Resins, ...	241
Winning and Refining of Fats and Oils, . .	228	Caoutchouc, Vulcanised Rubber, . . .	243
Properties and Uses of Fats and Oils, . . .	231	Varnishes—	
		Oil Varnishes, . . .	245
		Spirit Varnishes, . .	246

CHAPTER XI.

Soap and Candles.

Soap—		Candles—	
Raw Materials, . .	247	Tallow, Wax and Sperm Candles, . . .	250
Manufacture, Fitted Soap, Soft Soap, Toilet Soap, .	248	Hydrolysis of Fats for Stearin Candles, . .	252
		Glycerin, ...	255

CHAPTER XII.

Textiles and Bleaching.

Textile Fibres—		Wood Wool and Mineral Fibres, ...	262
Wool, Wool Fat, Yorkshire Grease, . .	257	Bleaching—	
Silk, Artificial Silk, . .	259	Wool and Silk Bleaching, .	264
Cotton, ...	260	Cotton, Linen, and Jute Bleaching, . . .	265
Flax, Hemp, Jute, . .	261		

CHAPTER XIII.

Colouring Matters, Dyeing and Printing.

General Principles—		Triphenylmethane derivatives, Nitrobenzene, Aniline, Magenta, . .	203
Dyestuffs defined, Theory of Dyeing, . . .	270	Phthalein Dyestuffs, .	292
Colouring Matters — Organic Synthetic Dyestuffs—		Azine Compounds, Magdala Red, Mauveine, Quinonoximes, Indamines,	302
Nitro-compounds, . .	273	Dyestuffs containing Sulphur, Methylene Blue, .	3
Azo-compounds, . .	273		
Quinone Derivatives, Alizarin, ...	278		

PAGE

Oxazine Colouring Matters—
Auramine, Tartrazines, 307
Aniline Black, Indulines, Safranines, . . . 311
Quinoline Derivatives, . 316
Natural Organic Dyestuffs—
Indigo, Artificial Indigo, . 319
Dyewoods, Logwood, Brazil Wood, Fustic, . 324
Lichen Colouring Matters, Litmus, . . . 326
Cochineal, Lac Dye, . 327
Mineral Dyes—
Chrome Yellow, Manganese Brown, Prussian Blue, ... 328

PAGE

Dyeing and Mordants—
General Principles, . . 329
Mordants, Basic Mordants, Acid Mordants, . . 330
Cotton Dyeing, . . 333
Wool Dyeing, . . . 335
Silk Dyeing, . . . 338
Jute Dyeing, . . . 339
Printing—
Cotton Printing; Steam, Pigment, Dyeing, Discharge and Resist Styles, 340
Wool Printing, . . 342
Water for Dyeing, . . 343

CHAPTER XIV.

Paper and Pasteboard.

Raw Materials—
Rags, Esparto, Wood, . 344
Manufacture of Paper Pulp—
Esparto Boiling, Recovery of Alkali, . . . 345
Mechanical and Chemical Wood Pulp, . . . 347

CHAPTER XV.

Pigments and Paints.

Mineral Pigments—White Pigments—
White Lead, Dutch, German and Precipitation Processes of Manufacture, 349
Zinc White, Barytes, Whiting, . . . 353
Blue Pigments—
Ultramarine, . . . 354
Prussian Blue, . . . 356
Smalt, Cobalt Blue, . . 357
Green Pigments—
Brunswick Green, . . 358
Chromium Greens, Copper Greens, Rinmann's Green, 359
Yellow Pigments—
Chrome Yellow, . . 360
Cadmium Yellow, King's Yellow, . . . 361
Red Pigments—
Red Lead, . . . 361
Vermilion, Antimony Vermilion, ... 362
Iron Pigments—
Red Oxide, Ochres, Siennas, Umbers, . . . 363
Organic Pigments—
Lampblack, Bone and Ivory Black, ... 364
Cochineal Carmine, Sepia, 365
Paints and Vehicles, . . 366

CHAPTER XVI.

Manufacture of Leather, Glue and Size.

	PAGE
Leather—Raw Materials—	
Hides and Skins,	367
Water,	372
Tanstuffs, Tannic Acid,	373
Preparatory Processes—	
Cleansing and Softening,	381
Unhairing,	382
Softening Processes,	384
Tanning Processes—	
Tanning with Tanstuffs, Sole Leather, Dressing Leather, Dyeing Leather,	386
Tanning with Mineral Salts, Alum Tanning, Chrome Tanning, Iron Tanning,	389
Tanning with Oils, Wash Leather,	391
Finishing Processes—	
Finishing Sole Leather,	392
Currying, Russia Leather, Patent Leather,	393
Theory of Tanning,	394
Gelatine, Glue and Size,	395

CHAPTER XVII.

Explosives and Matches.

Explosives—	
General Principles,	398
Gunpowder, Nitre,	400
Nitro-Explosives (High Explosives), Gun-cotton,	403
Nitroglycerin Explosives, Manufacture of Nitroglycerin, Dynamite, Blasting Gelatine, Cordite,	405
Other Nitro-explosives,	407
Matches—	
Phosphorus Manufacture,	408
Red Phosphorus,	410
Match Compositions,	411

CHAPTER XVIII.

Minor Chemical Manufactures.

Acids—	
Hydrofluoric Acid,	413
Boric Acid and Borax,	414
Arsenic Acid,	415
Oxalic and Lactic Acids,	416
Tartaric and Citric Acids,	418
Benzoic Acid, Salicylic Acid, Saccharine,	419
Salts—	
Chromates and Bichromates,	420
Manganates and Permanganates,	422
Sulphates, Copper Sulphate, Copperas, Alum,	423
Potash Salts,	426
Strontium Salts,	429
Halogens—	
Bromine, Iodine, Potassium Iodide,	430
Cyanogen Compounds—	
Potassium Cyanide, Prussiate of Potash, Sulphocyanides,	432
Solvents—	
Carbon Bisulphide, Carbon Tetrachloride,	434

CHEMISTRY

FOR

ENGINEERS AND MANUFACTURERS.

VOL. II.

THE CHEMISTRY OF MANUFACTURING PROCESSES.

CHAPTER I.

SULPHURIC ACID MANUFACTURE.

RAW MATERIALS FOR VITRIOL MAKING.

Sulphur.—**Native sulphur** occurs in rocky deposits of volcanic districts, notably in Sicily; it averages 20 per cent. of the total rock, but may reach as high a proportion as 80 per cent. It is obtained (1) either by a crude liquation process, consisting in igniting a heap of the rock (*calcarone*), and collecting that portion of sulphur which escapes combustion and flows out, or by melting out the sulphur (in the case of rich materials) by heating it in closed vessels by extraneous fuel; (2) by distilling the ore in iron retorts set obliquely; (3) by systematic extraction with carbon bisulphide, and subsequent distillation of the solvent. The nature of the apparatus for the third method may be gathered from the figure of an oil extractor (see *Oils*, Vol. II., Chap. X.); the process is also used for obtaining sulphur from gas-purifying masses (see *Destructive distillation*, Vol. II., Chap. III.).

Sulphur is obtained in small quantity by the distillation of pyrites, FeS_2, which gives up rather less than half its content of sulphur.

Recovered sulphur from alkali waste and gas liquor is dealt with under the corresponding heads.

Sulphur is put upon the market in the refined state, the refining being simply a process of distillation; the rapidly cooled

vapour (yielding the insoluble modification) is sold as **flowers of sulphur**. When cast into sticks, it is known as "**roll brimstone.**"

Pyrites is by far the most important source of sulphur for vitriol making; commercial grades contain about 50 per cent. of sulphur. **Smalls** are simply the broken fragments of pyrites, and need no separate comment.

Gas purifier mass (*spent oxide*) may contain 40 to 50 per cent. of sulphur, and thus ranks with pyrites smalls.

Nitrate of soda is sufficiently dealt with under *Artificial manures* (Vol. II., Chap. IV.).

Air and water are the other raw materials for vitriol manufacture.

SKELETON OF PROCESS OF VITRIOL MAKING.

In order to make clear the details of manufacture described below, the following outline of the process of vitriol making, as usually carried out, may be here given.

The sulphur in either of the forms used in practice (viz., pyrites, spent oxide, or elementary sulphur) is burnt in a kiln by the heat of its own combustion, and the sulphur dioxide, mixed with air, and nitrogen corresponding with the oxygen used in the combustion of the sulphur, meets nitric acid vapour, generated as described below, and immediately reacts with it, liberating oxides of nitrogen. This mixture of gases passes into leaden chambers where it meets with steam; a reaction resulting in the formation of dilute sulphuric acid occurs, in which all the constituents, save the nitrogen, are concerned. The latter gas has to be removed from the chambers by a draught, and in order to avoid the carrying away of the oxides of nitrogen, which, although taking part in the reaction, are regenerated in the course of it, a column—the Gay-Lussac tower—down which strong sulphuric acid trickles, is interposed between the chambers and the chimney. The oxides of nitrogen are absorbed by this sulphuric acid, and are re-introduced into the sphere of reaction in the leaden chambers by being expelled from the sulphuric acid by the heat of the gases from the pyrites kiln, which gases are caused to ascend the tower—the Glover tower—placed between the pyrites kiln and the leaden chambers; the sulphuric acid, containing oxides of nitrogen, from the Gay-Lussac tower, is allowed to trickle down this column, the oxides of nitrogen being driven off and carried into the first chamber.

PROCESSES AND PLANT.—For the production of the sulphur dioxide some furnace is necessary for burning the pyrites, sulphur, or other sulphur-containing material. The construction of this differs somewhat with the nature of the material to be burnt. **Pyrites burners** are of two forms—(1) burners for lump pyrites, and (2) burners for "smalls." These two are re-

quired, because in the crushing of pyrites, as mined, both lumps and dust ("smalls") are produced, which, if burnt together, would form an impervious layer, greatly impeding the proper admission of air. Burners for lump pyrites consist of fire-brick chambers, A (Fig. 1), about 6 ft. × 5 × 4 ft., with slightly sloping sides, set in pairs, and provided with a grate, B, made of iron bars of square section which can be rotated at will. The pyrites rests on this grate to a depth of 2 to 3 feet, and as it burns the iron bars are rotated, allowing the burnt ore to drop out. The burners are fitted with two doors, one at the top for charging the pyrites, and a smaller one lower down for adjusting the burning charge. In burning, not only has enough air to be introduced to oxidise both sulphur and iron of the pyrites, according to the equation—

$$2FeS_2 + O_{11} = Fe_2O_3 + 4SO_2,$$

but also sufficient to convert SO_2 into H_2SO_4 by the aid of the nitrous gases that act as carriers of oxygen (see p. 11). In the actual management of the burners, the two main objects to be attained are the conversion of as much of the sulphur as possible into sulphur dioxide, and the avoidance of the formation of clinker ("scars") due to the fact that defect of air allows of the production of the fusible sulphide, FeS. This latter object is achieved by stirring the charge through the lower door. As the complete combustion of the sulphur of the pyrites in practice cannot be effected without an excess of air more than enough to serve for the subsequent oxidation of SO_2 to H_2SO_4, the efforts of the manufacturer are directed to keeping the air supply as small as is consistent with the above conditions. It is found that the flue gases from burners using pyrites contain about 7 per cent. of SO_2, together with some SO_3 resulting from the formation and subsequent decomposition of sulphates of iron in the oxidation of the pyrites, and about 10 per cent. of oxygen, which serves for the conversion of the SO_2 into H_2SO_4. It is not practicable to roast out the whole of the sulphur from the pyrites, the burnt residuum usually containing from 2 to 3 per cent. as basic ferric sulphate, and the sulphates of metals such as zinc and copper, the oxides of which are stronger bases than is ferric oxide. In the case of cupreous pyrites, which are burnt and returned to the copper smelter, it is not desirable to burn the whole of the sulphur, as for the extraction of copper there should be present 1 to 1½ times its weight of sulphur, unless the ore be poor in copper and intended to be extracted by the wet way, in which case roasting as completely as possible is sure to leave enough sulphur in the ore (see *Copper*, Vol. I., p. 165).

Not only do the smaller fragments of crushed pyrites need to be burnt in furnaces different from those used for lump pyrites, but spent purifier from gas works (see *Destructive distillation*, Vol.

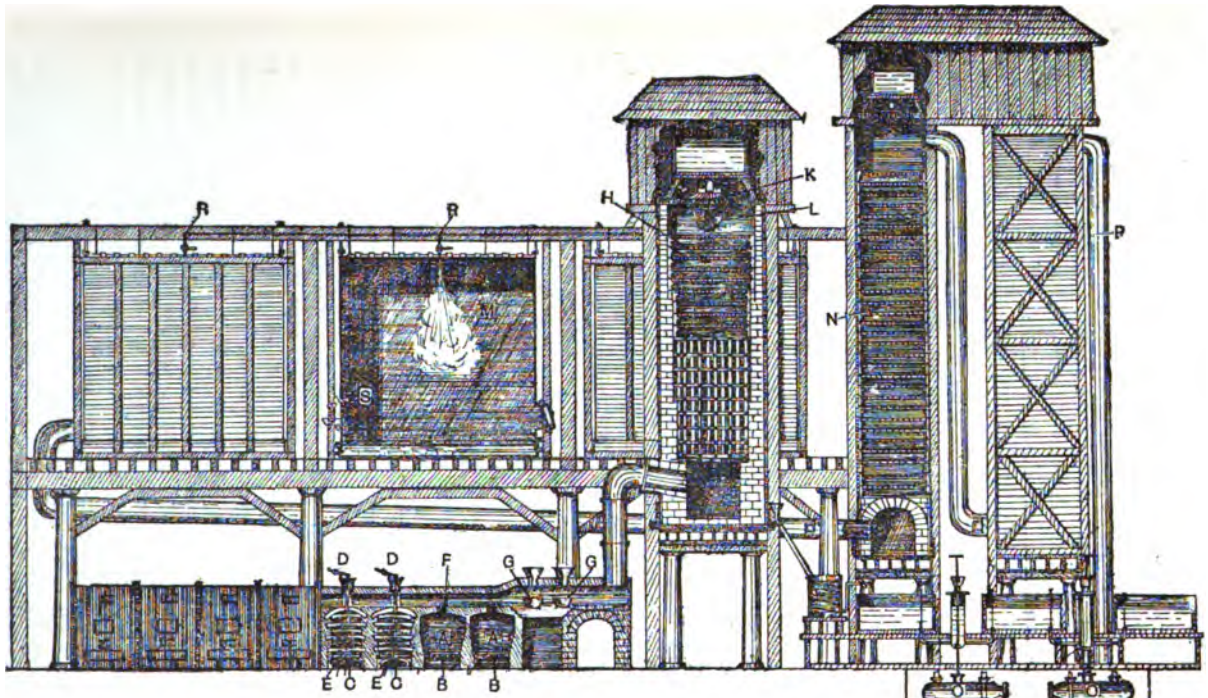


Fig. 1.—Plant for the manufacture of sulphuric acid.

A, A, Pyrites kilns; B, B, fire grates; C, C, smalls burners; D, D, hoppers for charging; E, E, shelves for the pyrites smalls, F, flue; G, G, nitre pots; H, Glover tower; K, distributor; L, flue leading to chambers; M, chamber shown in section across longer axis; N, Gay-Lussac tower; O, acid-egg; P, exit flue; R, R, steam jets; S, acid drip.

II., Chap. III.) has also to be treated in a similar manner. The burner for smalls must be so arranged that the material is spread in a fairly thin layer, inasmuch as the kiln form, described above, would be speedily choked. The **smalls burner** is shown at C in Fig. 1. It consists of a rectangular firebrick box provided with horizontal fireclay shelves, so disposed that the smalls can be raked from one to the next below by a rake inserted through the opening. The smalls are fed in through the hopper, D, and when they have been distributed on the shelves the combustion is started by the fire on the grate, E. The smalls, when once ignited, evolve sufficient heat to maintain the combustion. When the burner is working normally, the whole of the necessary air is admitted through the lowest door, and the smalls are only completely burnt on reaching the lowest shelf, at which stage the burnt material contains from 1 to 2·5 per cent. of sulphur. Various mechanical burners for pyrites smalls have been devised, the object in view being to keep the pyrites stirred, and thus constantly expose fresh surfaces to oxidation, but they have not met with extended application, as they tend to clog with the fine dust.

When vitriol is made from sulphur, the simplest form of burner consists of an iron tray, on which sulphur is thrown from time to time, and there volatilised and burnt. In better forms of burner, provision has to be made for the complete combustion of such sulphur as is sublimed. This is effected by the addition of firebrick towers into which a subsidiary supply of air is introduced to cause complete combustion. When sulphur instead of pyrites is used, the air is required to oxidise S only, and not Fe as in the latter case, whence it results that the exit gases are richer in SO_2 and poorer in N than those from pyrites burners. The difference is indicated by the fact that gases from sulphur burners contain 11 per cent. of SO_2 as compared with 7 per cent. from pyrites burners. The amount of free oxygen is about 10 per cent., the balance being of course nitrogen. Another source of SO_2, for the manufacture of sulphuric acid, is zinc blende (see *Zinc*, Vol. I., p. 181), which is roasted in muffle furnaces heated by generator gases and provided with heating channels for warming the in-coming air so as to insure the complete oxidation of the S of the blende. In order the better to attain this end, the roasting is done systematically, the ore being transferred from one muffle to the next through a series.

Sulphuretted hydrogen, such as is produced from alkali waste (see *Alkali*, Vol. II.) or by the neutralisation of crude ammoniacal liquor from gas works, can be burnt to SO_2 and water, and used as a raw material in the production of sulphuric acid.

Sulphur dioxide is frequently made by the methods described above for producing sulphurous acid and sulphites, which are much used in paper-pulp making (*q.v.* Vol. II.). Where a solution of

sulphurous acid is alone required, the kiln gases are scrubbed with a small amount of water (which soon becomes saturated), and are absorbed in cold water flowing down a coke tower. To prepare **liquid SO_2**, however, it is necessary to obtain the gas free from admixed nitrogen, in order that its partial pressure may be as high as possible. For this purpose the solution of sulphurous acid in water is heated in leaden retorts, and the SO_2 thus expelled is dried by scrubbing with vitriol, and is compressed in an ordinary gas compressor, about 2·5 atmospheres being required. The liquid SO_2 is collected in iron and copper cylinders and drums, and, for small quantities, in stout glass bottles. The liquid has a specific gravity of about 1·4, and boils under atmospheric pressure at $-10°$ C. $= 14°$ F. It is used as a convenient and compact source of the gas in many industries.

The chief **sulphites** commercially used are **sodium bisulphite**, $NaHSO_3$, prepared by saturating soda crystals with SO_2, and **normal sodium sulphite**, $Na_2SO_3 7H_2O$, which is prepared by adding sodium carbonate solution to a solution of the bisulphite. The bisulphite is the less soluble, and finds application as an antichlor. **Calcium bisulphite**, $CaH_2(SO_3)_2$, prepared similarly, is sold in solution for brewers' use as a disinfectant.

In the manufacture of sulphuric acid, however the SO_2 may have been produced, it is led by a flue, F (Fig. 1), common to a set of burners, to the Glover tower (*v.i.*). In this flue one or more (usually two) **nitre pots**, G, are set. These consist of cast-iron vessels, generally cylindrical, placed in the flue beneath hoppers through which the nitre (sodium nitrate) is charged in quantities of about half a cwt., sulphuric acid being introduced through S-shaped syphon tubes, which serve as traps, to decompose the nitrate and liberate nitric acid. The pots are fitted with a waste pipe, running through the wall of the flue, whereby the liquid *nitre-cake* ($NaHSO_4$) can be drawn off when the charge is exhausted. The heat of the burner gases, which have a temperature of about 300° C. $= 572°$ F., is also sometimes utilised for concentrating chamber acid (*v.i.*). Much dust is liable to be deposited in the flue, particularly when pyrites smalls and arsenical ores are burnt. Where this deposit is large, it is needful to lead the flue into a dust chamber before it enters the Glover tower. This chamber is an enlargement of the flue, provided with baffle plates, in which the rate of the current of gases is diminished, and the stream mechanically broken up so that the dust is thrown down. In works where chamber acid alone is made, and the Glover tower dispensed with (*v.i.*), it is necessary to cool the burner gases before they enter the lead chambers, which is effected by greatly prolonging the burner flue, in which case the dust deposits in this prolongation. The flue dust consists mainly of burnt ore mechanically carried over, mixed with volatile impurities, chief among these being arsenious oxide and sulphuric acid (from the decomposition of sulphates of iron formed in roasting the pyrites).

The Glover tower, H (see Fig. 1)—the function of which, in the reactions involved in the manufacture of vitriol, will be dealt with later—is a strong structure, square or circular in section, with leaden walls lined with refractory and acid-proof firebrick, and filled with some acid- and heat-resisting material, such as flint or firebrick, arranged so as to distribute evenly liquid trickling down the tower; it is supported on brick arches, underneath which the pyrites flue enters the tower. The upper part of the tower, where the temperature is lower, may consist, as shown in the figure, of a plate column such as that described under the head *Chambers*. At the top of the Glover tower is a tank containing the chamber acid and the nitrous vitriol from the Gay-Lussac tower (*v.i.*); this tank supplies a distributing arrangement, such as a lead or glass wheel, K, worked by the reaction of the acid flowing from its radial arms. The exit pipe, L, for the gases which ascend the tower is at the top, and is connected with the first chamber.

Vitriol chambers are invariably made of lead—generally of a thickness corresponding with a weight of about 6 lbs. per square foot—and consist of rectangular "curtains" standing in "saucers" which are large, flat trays, the edges of which are turned up to a height of 12 to 15 inches. The sheets of lead composing the curtain, and those of which the saucers are made, are autogenously soldered ("burnt") by means of a hydrogen flame fed with a blast of air (see Vol. I., p. 34), and are fastened to the framework of wood which supports them by lead straps—themselves "burnt" on to the lead—attached to the wood by nails coated with lead. The whole arrangement resembles a box with a loosely-fitting lid turned upside down, and is shown in section across the longer axis of each at M. The whole is gas tight, on account of the saucer containing enough acid to seal the edges of the curtain. The chamber is carried on piers to allow of inspection and repair on all sides. The space below is utilised for the pyrites burners. The number of chambers and their size vary with the practice of different works. Usually, from two to four are used, and the size varies from 100 to 130 feet × 25 to 30 feet × 16 to 20 feet in height; it generally being supposed that about 20 to 25 cubic feet of space are required for each pound of sulphur burnt per day. The chambers are connected by lead tunnels, and the last of the series communicates with the bottom of the Gay-Lussac tower. Instead of relying on mere chamber space for the mixing and reaction of the gases, it has been proposed to use smaller chambers, and to interpose plate columns, up which the gases must pass in going from one chamber to the next, whereby an economy of chamber space is possible. These columns consist of a lead-lined tower fitted with horizontal stoneware plates, which are perforated, each perforation having raised edges and being surrounded by ridges, so that there may be always a little pool of liquid ready to overflow and drop through the perforation on to the plate next below, which is so placed that

the drop does not fall through a hole, but on to the surface of the plate; the arrangement is made clear by Fig. 2.

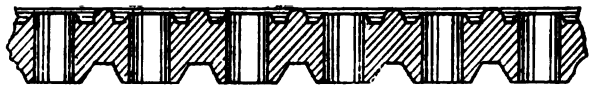


Fig. 2.—Perforated stoneware plate for plate columns.

Much liquid condenses in this column, and this aids the occurrence of the reactions necessary for the preparation of sulphuric acid, which are described below. These Lunge-Rohrmann plate columns, as they are termed, are occasionally substituted for ordinary Glover and Gay-Lussac towers.

The **Gay-Lussac tower,** N, is arranged like the Glover tower, and is of similar dimensions, but usually somewhat higher—*e.g.*, about 35 to 40 feet in height. A cistern at the top contains vitriol of specific gravity 1·75, which is raised to this position from the "acid egg" shown at O in Fig. 1. The method by which it is raised involves the use of no moving parts, compressed air being forced into the egg, and driving the acid up the pipe leading therefrom to the tank at the top of the Gay-Lussac tower. The acid flows from the cistern into a distributor similar to that used for the Glover tower, and already described. Where two Gay-Lussac towers are employed, the gases pass from the top of the first into the bottom of the second. In either case, a proper draught is secured by a pipe, P, running from the top of the Gay-Lussac tower to a chimney shaft. Inasmuch as the acid which has passed down the Gay-Lussac tower has to be raised to the top of the Glover tower by an acid egg like that already described, it is customary to build the towers side by side.

Manufacture of Nitric Acid.—In those vitriol works in which nitric acid is used as such (*v.i.*), instead of being generated on the spot in nitre pots as described above, an apparatus for its production necessarily forms a part of the plant. As this is similar to the plant employed by makers of this acid for other purposes, it will be described here. In all cases, it is made by heating sodium nitrate with strong sulphuric acid in cast-iron retorts. In English works these are generally horizontal cylinders, 5 feet × 2 feet, closed at each end by a sandstone slab (Yorkshire flags), one end being permanently affixed and provided with an exit pipe for the acid vapours, the other end serving as a charging door. Nitric acid has but little action on the iron, provided it be strong; if weak, a considerable action occurs. For this reason the whole of the retort should be kept hot to prevent the aqueous acid condensing on its upper part, a proceeding preferable to lining the upper part with firebrick, as is sometimes practised. The high temperature of the upper part of this still is secured by an appropriate setting of the cylinder in its furnace. The quantity of nitric acid obtainable

from any given weight of sulphuric acid depends primarily upon the temperature employed. Thus, if the temperature be comparatively low, the reaction takes place between equal molecular proportions of sodium nitrate and sulphuric acid. Thus—

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4,$$

whereas when it is higher two molecules of nitric acid are liberated by one of sulphuric,

$$2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4.$$

In practice it is not economical to use proportions complying with either of these equations. For the first, an undue amount of sulphuric acid is needed,* and in the second case the high temperature decomposes much of the nitric acid as soon as it is formed, and, moreover, the resulting sodium sulphate is solid, and even at high temperatures is difficult to remove from the retort. Furthermore, it is not customary to use the strongest commercial vitriol (specific gravity 1·84) because this has a tendency to dehydrate the nitric acid, resulting in the production of oxides of nitrogen. The sulphuric acid actually employed is often of specific gravity 1·72, and is used to the extent of about 25 per cent. in excess of that required by the second equation, given above. In this case the residue in the retort ("nitre-cake") is a mixture of Na_2SO_4 and $NaHSO_4$, and is sufficiently liquid to run out when the charge is worked off. The charge consists of one and a-half cwt. of sodium nitrate (95 per cent. $NaNO_3$) and about an equal weight of sulphuric acid of specific gravity 1·72. The form of retort most in vogue on the Continent, is a cast-iron cylindrical pot 5 ft. by 5 ft., with a wide neck fitted with a cover, the whole being enclosed in a furnace so that condensation may not take place at any part. A tube at the bottom of the retort serves for running off the nitre-cake, and another at the shoulder as an exit for the acid vapours.

The apparatus employed for condensing the acid usually consists of a number of two-necked stoneware Woulfe's bottles. The acid which condenses in the first of these is the strongest, but the most impure, containing splashings from the retort and oxides of nitrogen. That at the far end of the series contains chlorine (from the chloride present in commercial sodium nitrate), and is comparatively weak. Any acid still uncondensed is caught in a tower or plate column, which, in the case of a plant attached to a vitriol works, is fed with sulphuric acid (specific gravity 1·75), and the resulting nitrous vitriol used in the Glover tower. Otherwise the tower is fed with water. The crude nitric acid when first condensed is red from the presence of oxides of nitrogen. For some industries this is an advantage, and indeed a so-called "nitrous

* In soda works ample vitriol can be used with economy, for the residue of the nitric acid still goes to the salt-cake furnace, and is there utilised to the full.

acid" is made by the addition of reducing substances—*e.g.*, starch and sulphur—to the charge. Where a colourless acid is required, however, the red acid is "bleached" by warming and blowing air through it, the gases evolved being caught in the tower mentioned above. When the acid is used in vitriol works, this refining is unnecessary.

The condensing process just described has several defects—*e.g.*, the liability to fracture of the condensing pots, and the contamination of a great part of the acid with oxides of nitrogen.

Moreover, the distillation takes place slowly, and the yield of strong acid falls considerably below the theoretical limit, owing to

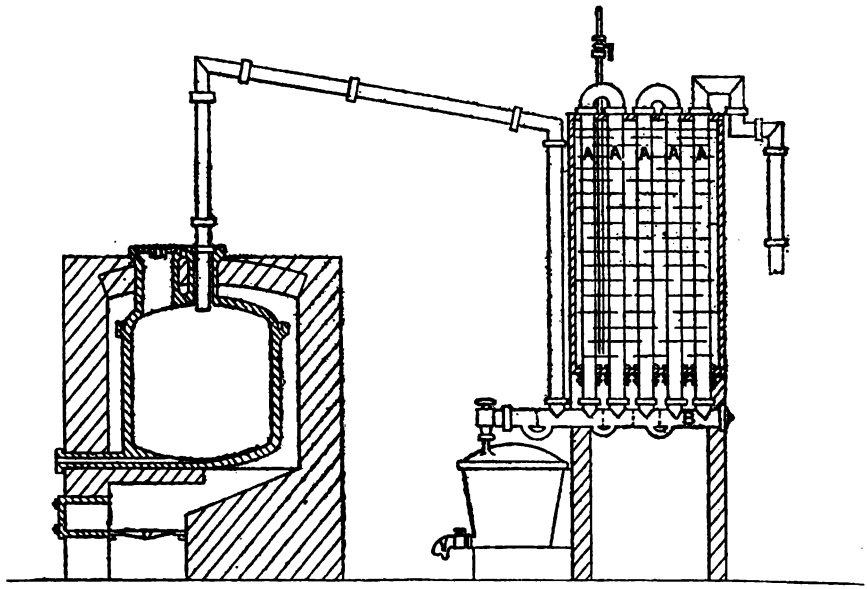


Fig. 3.—Nitric acid still and condensers.

the fact that the acid is not collected fractionally. These difficulties are said to be overcome by Guttmann's method of condensation. His condensers (see Fig. 3) consist of pairs of stoneware pipes, A, A, A, very thin in the walls, to aid condensation, and connected at the top by ∩ bends, and inserted at the bottom into a receiving pipe, B, with diaphragms between the legs of each bend, so that the condensed acid collects and can be drawn off out of contact with the still uncondensed gases. The final exit gases are caught in a plate tower. The system is said to be particularly adapted for the manufacture of the strongest nitric acid, free from oxides of nitrogen, such as that required for the manufacture of explosives.

Several grades of nitric acid are prepared for industrial use. Common **aqua fortis** is a dilute acid, and of specific gravity 1·3; it contains about 45 per cent. of HNO_3. It is used for parting gold and silver, for preparing silver nitrate and for pickling metal goods. A stronger acid, of specific gravity 1·42, containing 69 per cent. HNO_3, is also employed for similar purposes. This corresponds with the hydrate $2HNO_3,3H_2O$, and distils unchanged at 120° C. = 248° F. at ordinary atmospheric pressure. A stronger acid of specific gravity 1·5, containing 92 per cent. of HNO_3, is also prepared, and is employed for nitration (see *Explosives*, Vol. II., Chap. XVII.). This acid boils at 86° C. = 187° F. with partial decomposition into water, oxygen, and oxides of nitrogen, so that it cannot be distilled unchanged at the ordinary pressure. The chief impurities in nitric acid, as commonly made, are sulphuric acid and sodium sulphate, chlorine, oxides of nitrogen, iodic acid and perchloric acid (from iodate and perchlorate in the sodium nitrate), and iron.

Conversion of SO_2 into H_2SO_4.—The SO_2, produced as already described in the pyrites burners, passes into the Glover tower in company with nitric acid vapour from the nitre pots, and sufficient oxygen (derived from the excess of air necessary to burn the pyrites). The reaction of SO_2 with nitric acid takes place according to the following equation:—

$$2SO_2 + 2HNO_3 + H_2O = 2H_2SO_4 + N_2O_2.*$$

The reactions that occur in the Glover tower will be appreciated later, and will be referred to again.

As soon as the gases, consisting of SO_2, air, and N_2O_3, reach the chambers, they come in contact with steam, which is injected by the jets (R, Fig. 1) supplied from a boiler. When fuel is dear, water-sprays forced under pressure through platinum nozzles on to a platinum button, so as to "pulverise" the jet, have been used, but are liable to the objections that they cool the chambers below 40° C. = 104° F.—the minimum temperature for satisfactory working—and neither aid the draught nor promote the mixing of the chamber gases. The most probable explanation of the formation of sulphuric acid from these gases, and of the way in which the oxide of nitrogen serves as a carrier of atmospheric oxygen to the SO_2 is, that the SO_2, N_2O_3, O, and H_2O combine to form **nitrosyl-sulphuric acid**, according to the equation—

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2\begin{cases}OH\\O(NO)\end{cases}.$$

* It is stated by Ramsay that N_2O_3 can only exist in the liquid state, and becomes $NO + NO_2$ on evaporation. In this case, it could not be liberated under the conditions obtaining in vitriol making; the equation must, therefore, be modified thus—

$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO.$$

Corresponding alternative equations will be quoted for the reactions taking place at other stages of the process.

The substance thus produced may be regarded as sulphuric acid in which an atom of hydrogen of one of the hydroxyl groups has been replaced by the radicle (NO). In the event of the atmosphere of the chambers being unduly dry, nitrosyl-sulphuric acid may be actually deposited as a white mass ("chamber crystals"). In contact with more water, however, it splits up thus—

$$2SO_2(OH)(NO_2) + H_2O = 2H_2SO_4 + N_2O_3,$$

the cycle of changes being then repeated.*

It must not be supposed that the reactions in the vitriol chamber constitute such a regular cycle as has been indicated. Variations depending upon alteration of conditions, such as the relative mass of one or other of the reacting gases at any particular part of the chamber, and the temperature prevailing in different parts (portions near the wall being lower in temperature than those in the centre of the chamber) undoubtedly occur. The main point to be comprehended is, that one or more of the intermediate oxides of nitrogen serve, by dint of their chemical mobility, as carriers of oxygen from the air to SO_2. The equations formerly supposed to represent these changes illustrate this fact in its simplest form—

$$NO + O = NO_2,$$
$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO,$$

the cycle being then repeated.

However the sulphuric acid may be generated, it forms as a mist, which gradually rains down upon the bottom of the chamber, constituting the chamber acid referred to hereafter. On account of the need for thorough intermixture of the reacting gases, and of the condensing influence of a considerable surface upon them and upon the mist of sulphuric acid formed, it is found inexpedient to use one large chamber, two or more of moderate size being preferable, and, recently, small lead chambers, or even plate columns between larger chambers, as referred to above, have been tried with satisfactory results. In any case, the cubic content of the chambers must be great (*v.s.*), because a large volume of inert nitrogen from the air has to be handled, and a rapid current of the gases is undesirable, as prohibiting the proper fulfilment of their interactions. In the last chamber, an excess of air and

* Adopting the view that N_2O_3 does not exist at the temperature of the chamber (above 40° C. = 104° F.), the equation would be—

$$2SO_2 + 2NO_2 + O + H_2O = 2SO_2(OH)(NO_2).$$

The decomposition of this substance then takes place, by its reacting with a further quantity of SO_2 and water, thus—

$$2SO_2(OH)(NO_2) + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

The nitrogen dioxide is then regenerated by combination with oxygen—

$$NO + O = NO_2.$$

nitrous gases and but little SO_2 should be present. The excess of air used to burn the pyrites (*v.s.*) should suffice for the complete final conversion of NO into N_2O_3 or NO_2, as otherwise the recovery of this gas cannot be effected in the Gay-Lussac tower, into which the exit gases from the chambers pass.

The only permanent gas necessarily remaining after the formation of H_2SO_4, is the nitrogen of the air. But for the presence of this gas, the manufacture of vitriol might almost be conducted in a closed space. Failing pure oxygen cheap enough to be used instead of air, it is necessary to provide some means of collecting the nitrogen oxides, which would otherwise be carried away with the nitrogen which escapes up the chimney stack. This is the more requisite as the nitrate employed is the most costly reagent used by the vitriol maker. In good practice, 3 to 4 parts of sodium nitrate are needed per 100 parts of sulphur burnt, this being entirely owing to the unavoidable loss, even when a Gay-Lussac tower is used. It will be understood that in an ideal plant working with a perfect cycle of reactions, no nitrate after the first batch would be needed, but this state of things is never approached, not only on account of the mechanical loss by escape at the exit flue, and by dissolution in the chamber acid (in works where chamber acid is used without concentration in the Glover tower), but also by reduction of a portion of the higher oxides of nitrogen to nitrous oxide and nitrogen, which are unabsorbed in the Gay-Lussac, and still further by some nitric oxide escaping conversion into higher oxides in the last chamber, and being, therefore, unabsorbed in the Gay-Lussac. The Gay-Lussac tower has been already described. The vitriol flowing down it meets the exit gases, and absorbs therefrom the N_2O_3 * found in the last chamber, combination ensuing with the production of nitrosyl-sulphuric acid, according to the equation—

$$2H_2SO_4 + N_2O_3 = 2SO_2(OH)(NO_2) + H_2O.$$

The quantity of vitriol required for this purpose is considerable, amounting to about half the make of the chambers, because, if it be allowed to absorb too much N_2O_3, giving a product unduly rich in N_2O_3, a portion of the latter is likely to escape. It must have a specific gravity of at least 1·72, weaker acid absorbing badly. The saturated acid ("nitrous vitriol") running out at the foot of the Gay-Lussac is pumped by means of an "acid egg" to the top of the Glover, and is there distributed and allowed to flow down the tower in the manner already described.

The nitrous vitriol, mixed with the chamber acid, meets the ascending burner gases and gives up its N_2O_3, which is carried into the first chamber, reacting with SO_2 and H_2O in the way previously mentioned. The vitriol flowing down the Glover is thus denitrified,

* Compare footnote, p. 11, for the doubts cast on the existence of N_2O_3 at the temperature of a vitriol chamber.

and at the same time concentrated by the heat of the burner gases. A portion is cooled in leaden worms, and returned to the Gay-Lussac to act as an absorbent of N_2O_3, and the remainder is concentrated, or used without concentration, as may be required.

It is usual on the Continent to substitute nitric acid which has been made by a separate plant (*v.s.*) for that evolved from the nitre pots used in English practice. Where a Glover tower is employed, nitric acid is passed down the tower, together with the chamber acid, and is there decomposed according to the equations given on p. 11. In the absence of a Glover tower, the nitric acid is run into the first chamber, but to avoid the corrosion of the lead it is received on a cascade of glass or stoneware, on which it is spread out in a thin layer, becoming entirely decomposed by the entering burner gases before it reaches the floor of the chamber. The advantage of the use of nitric acid in place of nitre pots is that the regulation of the quantity of oxides of nitrogen in the chambers can be more easily effected according to the exigencies of working. Another plan for making good the loss of nitrate consists in introducing sodium nitrate into the Glover, but in this case the resulting vitriol is contaminated with sodium sulphate.

The acid which collects on the floors of the chambers **(chamber acid)** must be continually tested during the working of the process, to ascertain its specific gravity. Should this exceed 1·625, the lead is unduly attacked, and the acid retains considerable quantities of the oxides of nitrogen. The collection of the samples for the test is performed by means of leaden rain-gauges (see S, Fig. 1) situated in different parts of each chamber, and connected with the outside by means of a lead siphon pipe. Each of these "drips" is provided with an hydrometer, whereby the specific gravity of the acid is determined, and the amount of steam to be admitted ascertained. Usually 1 part by weight of sulphur burnt requires $2\frac{1}{4}$ parts of water as steam. The acid from the drips is generally stronger than that from the bottom of the chambers ("bottom acid"), chiefly because it is taken from the centre of the chamber where the steam supply is smaller than at the sides. It is customary to connect the saucers of the various chambers by pipes, and to draw off the chamber acid by means of a lead box connected by a wide pipe with one of the chambers, and provided with an exit pipe which can be opened or closed by a plug operated by a suitable handle. In order to control the production of SO_2 in the burners, and the consumption of sodium nitrate, the chambers are provided with sights, through which their working can be judged by observing the colour of the gases they contain. The gas in the last chamber should be fully red from the presence of an ample excess of nitrogen oxides and of oxygen. The Gay-Lussac tower is also provided with sights, and as a further check the exit gases are systematically collected and analysed. According to the regulations of the Alkali Act, the

exit gases must not have an acidity greater than that corresponding with the presence of 4 grains of SO_3 per cubic foot, but in good practice the amount escaping is considerably below this limit, being, viz., about 1·5 grains per cubic foot.

CONCENTRATION.—The chamber acid is strong enough for some purposes, but concentration must generally be carried out. The passage of the chamber acid down the Glover tower, concentrates it to a specific gravity of 1·72, but usually contaminates it with iron salts (derived from the dust from the pyrites burners), so that its further concentration in retorts (*v.i.*) cannot be economically effected on account of the separation of such impurities. However, for alkali making by the Leblanc process, Glover acid is suitable. Where a Glover tower is not used, or in cases where it is desired to avoid the contamination referred to above, concentration to the same specific gravity is performed in lead pans, which are either heated by furnace gases passing over the surface of the liquid (in which case the acid is contaminated with flue dust, thus acquiring a brown colour to which the acid owes its name, "**brown oil of vitriol**," "B.O.V."), or by bottom heating which produces a purer acid. On account of the tendency of the lead pans to buckle, by unequal expansion, it has been recently proposed by Carulla to insert a sheet of copper between them and their iron setting, the difference between the coefficient of expansion of lead and copper being smaller than that between the coefficient of expansion of lead and iron; at the same time the high conductivity of copper for heat contributes to a more even heating. High-pressure steam in lead coils is also used. The concentration in lead pans cannot be carried further than that corresponding with a specific gravity of 1·72, as the lead is seriously attacked when this strength is exceeded. With regard to the quality of the lead of which these pans and the leaden chambers should be constructed, it may be said that the purest lead is the best. The greater the content of the nitrogen oxides in the acid, the more the pans are attacked.

When a higher degree of concentration is needed, the acid is boiled down in glass or platinum stills. The former are large glass retorts, about 3 feet in height and 21 inches in diameter, set in sand baths and heated from below. Though their first cost is small, frequent breakages make the system an expensive one. A better method is that of concentrating in very shallow flat-bottomed platinum stills which are provided with internal partitions so that the acid traverses a considerable distance inside each still, and can be run through the stills continuously. The platinum is considerably attacked during concentration, to an extent largely dependent upon the impurities present in the vitriol, nitrous vitriol being particularly active. As much as 3 grammes of platinum per ton of acid of specific gravity 1·84, containing 93 per cent. H_2SO_4, is dissolved when a little nitrous acid

is present. To diminish this loss, stills of a 10 per cent. iridio-platinum alloy have been tried, but abandoned as being too brittle. Better success has attended the use of a plan devised by Heraeus, in which a thin layer of gold is alloyed with and rolled hot into a sheet with platinum, the gold lining of retorts made of this material resisting well. To economise platinum, the heads of the stills are made of lead, double walled, and cooled with water, by which means they resist the attack of the weaker acid distilled off during concentration. Recently, various methods of systematic concentration have been introduced, consisting essentially in a series of vessels, of glass or refractory stoneware, or of shallow platinum troughs, arranged terrace-wise so that the acid to be concentrated flows down the series, and is either heated by a flue below the vessels, or by furnace gases passing over them, in a direction the reverse of that of the flow of the acid. Acid already concentrated to a specific gravity of 1·84 can be further evaporated in cast-iron vessels (as obtains in American practice) without attacking them.

There is a limit to the concentration of sulphuric acid by boiling, for when a strength of 98 per cent. H_2SO_4 is reached, the acid dissociates considerably into H_2O and SO_3. Acid of higher strength, approximating to what is commercially known as "monohydrate" —*i.e.*, pure H_2SO_4—can be prepared by freezing ordinary concentrated acid of 96 to 97 per cent. strength, by exposing the acid in sheet iron cells immersed in a solution of calcium chloride cooled to $-20°$ C. $= -4°$ F., superfusion being averted by the addition of fragments of frozen sulphuric acid. The blocks of frozen acid are removed by immersing the cells for a few seconds in hot water, and are broken up, drained in a hydro-extractor, packed and melted in iron drums, in which the acid can be transported. So-called "solidified sulphuric acid" consists either of kieselguhr saturated with vitriol or a semi-solid mass made by heating mixtures of sulphuric acid with sodium sulphate, containing more available sulphuric acid than does sodium bisulphate. These preparations are used for convenience of transit, and are made ready for use by addition of water, in which case the kieselguhr mixture has to be allowed to settle, to deposit the silica that has been used as an absorbent.

PURIFICATION.—Chamber acid contains oxides of nitrogen, lead sulphate, and arsenic (when pyrites has been used). During its passage down the Glover tower it takes up iron (*v.s.*). The most objectionable of these impurities is the arsenic, which passes into the hydrochloric acid produced in the manufacture of salt cake, and unfits it for many applications. Arsenic is eliminated by passing H_2S through the chamber acid and allowing the precipitated As_2S_3 to settle. Arsenic-free vitriol is, however, best made from brimstone, native or recovered (see *Sulphur*, Vol. II., p. 1). Oxides of nitrogen are got rid of by heating the acid with ammonium sulphate before it goes into the platinum stills, where this

impurity would cause corrosion (*v.s.*). The equation representing the reaction is

$$N_2O_3 + (NH_4)_2SO_4 = N_4 + H_2SO_4 + 3H_2O.$$

Iron and lead are allowed to remain in ordinary vitriol. When a less impure acid is required, the comparatively weak distillate from the platinum stills is concentrated and utilised, or, for laboratory use, distillation in glass is adopted.

The specific gravity of sulphuric acid reaches a maximum at a strength of 97·7 per cent., when it has the value of 1·8415 (15° C. = 59° F.). It follows, therefore, that the statement of the specific gravity of a sample of vitriol (even disregarding the influence of impurities such as lead sulphate) does not define its strength when this is between 95 and 100 per cent. On account of this, highly concentrated sulphuric acid should be bought on analysis and not according to its specific gravity.

NORDHAUSEN OR FUMING SULPHURIC ACID.—The first form in which sulphuric acid was commercially manufactured was as fuming sulphuric acid at Nordhausen in Saxony, and the manufacture has continued but little changed to the present day. Ordinary vitriol is still called in Germany **English sulphuric acid,** in contradistinction to the fuming acid. The production of fuming sulphuric acid depends on the fact that the sulphates of all but the strongest bases—*e.g.*, the alkalies and alkaline earths—are decomposed by heat, many of them yielding sulphuric anhydride (SO_3) as the main product of the decomposition. The sulphates actually employed are, as yet, only those of iron and aluminium, which are dissociated at a moderate temperature. The simplest typical case of the decomposition of a sulphate, by heat, with the production of SO_3 is that afforded by ferric sulphate, thus—

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

In practice, however, ferrous sulphate is the raw material of the manufacture. The salt is dried to expel its water of crystallisation, during which process it becomes partially oxidised by air, with the formation of basic ferric sulphate. The basic ferric sulphate splits up according to the equation given above, save that the Fe_2O_3 bears a larger proportion to the SO_3, and the $FeSO_4$ decomposes in the following manner:—

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

Formerly, when dehydration was not carried out, both sulphuric acid and SO_3 were distilled over, the product being common Nordhausen acid. Nowadays the raw material is obtained by weathering "vitriol shales," such as are found in Bohemia. They already contain some sulphates, together with about 15 per cent. of pyrites, with 2 to 3 per cent. of alumina, most of the remainder consisting of silica. When this mineral is exposed to the air, the

iron pyrites oxidises to ferrous sulphate and sulphuric acid, which latter combines with the alumina and other bases; the ferrous sulphate further oxidises to basic ferric sulphate. The weathered mineral is lixiviated, and the liquor is concentrated to a syrup, which solidifies on cooling to a yellowish-green mass, which is finally calcined and known as "vitriol stone." In whatever way the sulphates of iron or aluminium are obtained, they are heated in small clay retorts to redness, the distillate being received in long stoneware flasks containing a small quantity of water or a weaker fuming acid from a previous operation. By redistilling the distillate at a low temperature, the **sulphuric anhydride** passes over first, and by condensing the vapour in already fuming acid, or by itself, a Nordhausen acid of any desired strength can be obtained. The best commercial product contains 98 per cent. of free SO_3.

The residue in the retort (**caput mortuum**) constitutes the colcothar or rouge of commerce (see *Pigments*, Vol. II., Chapter XV.). Its content of Fe_2O_3 depends on the nature of the raw material.

H_2SO_4 and SO_3 mix in all proportions, but also form a fairly definite solid compound, corresponding with the formula $H_2S_2O_7$ (*i.e.*, $H_2SO_4SO_3$), commercially known as solidified oil of vitriol. Sodium bisulphate, $NaHSO_4$, gives off water when heated, and forms $Na_2S_2O_7$, which, at a temperature of 600° C. = 1,112° F., breaks up into Na_2SO_4 and SO_3, a reaction which has been used for the production of the latter substance, nitre cake serving as the raw material. Numerous attempts have been made to take advantage of the combination which occurs between sulphur dioxide and oxygen when heated in contact with such substances as finely-divided platinum and the oxides of iron, chromium and copper, but they have not proved commercially successful. It is stated, however, that the SO_3 present in burner gases (*v.s.*) can be economically collected. SO_3 and fuming sulphuric acid (*anhydrosulphuric acid*) find application in the dissolution of indigo as indigo sulphonic acids (see *Colouring Matters and Dyes*, Vol. II., Chapter XIII.), for purifying ozokerite, and in the manufacture of synthetic dyes. For some other purposes it is preferable to oil of vitriol by reason of its smaller content of water, and consequently greater sulphonating action (see *Dyes*, Vol. II., Chapter XIII.).

CHAPTER II.

MANUFACTURE OF ALKALI AND ITS BYE-PRODUCTS.

I. LEBLANC PROCESS.

RAW MATERIALS.—The raw materials used in the manufacture of soda by the Leblanc process, which dates from 1791, are salt, vitriol, calcium carbonate, and small coal, the process consisting essentially in converting salt into sodium sulphate and heating this with limestone and small coal, whereby it is converted into sodium carbonate.

Salt.—This substance occurs as a mineral in beds of rock salt in widely-scattered districts, and in solution as brine in sea-water and salt springs. The most important deposits of rock salt in England are those in Cheshire and Worcester, though recently considerable quantities have been found at Middlesbrough in Durham. In Cheshire and in Ireland (Carrickfergus) the rock salt is mined. The rock salt is dark red to bright yellow in colour (owing to the presence of the ferruginous marl associated with it). The purest specimens are colourless, and approximate in composition to pure sodium chloride—a characteristic Cheshire sample containing 98·3 per cent. NaCl together with 0·05 per cent. $MgCl_2$ and 1·65 per cent. $CaSO_4$.

The presence of calcium sulphate is usually explained by the supposition that the salt is the product of the evaporation of inland seas, from which calcium sulphate and sodium chloride, as respectively the most insoluble and the most abundant salt present in sea water, would be thrown down, the mother liquor containing more soluble and less abundant salts (see *Stassfurt salts*, Vol. II., Chap. XVIII.). Where natural waters have accumulated in strata adjoining those of rock salt, a boring made through the superincumbent strata will bring the water in contact with the salt and produce a saturated solution, which can be pumped up and evaporated. Where no water is naturally present, the wells may be artificially supplied therewith, and the brine pumped as mentioned above. Water is naturally available for the Cheshire deposits, while it is artificially supplied in the Middlesbrough district. The method of pumping brine (although this

necessitates subsequent evaporation) is cheaper than mining solid salt, where the depth of the salt bed is great. The composition of the brine may be gathered from the following analyses :—

	Cheshire.	Worcester.
NaCl, . .	25·222 per cent.,	22·452 per cent.
$CaSO_4$, . .	0·391 ,,	0·387 ,,
Na_2SO_4, . .	0·146 ,,	0·390 ,,
$MgCO_3$, . .	0·107 ,,	0·034 ,,

The degree of concentration of these brines may be gathered from the fact that a saturated solution of salt in water contains 26·5 per cent. of NaCl. The brine, however obtained, is evaporated in salt-pans made of boiler-plate and set over the flues of a series of furnaces which vary somewhat in size, according to the quality of salt to be produced. For the manufacture of fine-grained or lump salt, the pans are from 25 to 35 feet long, 20 to 24 feet wide, and 15 to 18 inches deep. The brine is boiled, the temperature reaching 107·5° C. = 225° F. The salt which separates is raked to the sides of the pan, and is lifted out from time to time on perforated skimmers. The crystals are thrown into wooden boxes, where they agglomerate on account of the crystallisation of the brine adhering to them. The blocks in which salt is commonly sold as table salt are obtained in this way. They receive a final stoving before they are sent into the market. Common salt is a coarser grade used for manufacturing purposes, and is made at a lower temperature (in somewhat larger pans), so that the crystals are larger and more impure. The temperature of evaporation varies from 60° to 80° C. = 140° to 176° F.

The crystals are treated as in the preceding case, but are merely drained on the shelves (hurdles) surrounding the pans. "Fishing salt" is made at a still lower temperature, and in still larger pans. The temperature is from 35° to 60° C. = 95° to 140° F., and the drawing of the salt takes place at less frequent intervals. "Bay salt" is made in the largest pans, sometimes over 130 feet long by 28 feet broad, and at a temperature of 35° to 50° C. = 95° to 122° F. The grain of the salt depends not only on the temperature of evaporation, and on the time allowed for crystallisation, but also on the influence of impurities in the mother liquor. So marked is this influence that it is customary to add some colloid substance —*e.g.*, gelatine or glue—to the pan when the smallest crystals are required, the process being known as "poisoning the pan." "Hopper salt" is an accumulation of crystals resembling a four-sided hopper, and is produced by the addition of a little alum to the pan. The calcium sulphate and magnesium carbonate in the brine, deposit in the salt pans, causing a scale which has to be occasionally picked out and frequently causes the pan to leak by overheating. Thus it nearly always happens that brine from one or other of the pans finds its way into the fire beneath, where

the sulphurous gases from the coal cause an evolution of HCl. This frequently becomes a nuisance, and the chimney gases are, therefore, under the supervision of the Inspectors under the Alkali Act. Brine is also concentrated on the Continent by being allowed to trickle over stacks of brushwood ("graduation towers") whereby water is evaporated by wind and sun, and fuel is saved; the evaporation of the saturated brine is completed in salt-pans as described above.

Sea-water is used as a source of salt, both in hot and cold countries, where its evaporation may be effected without the use of fuel, the expense of which is too great to allow its employment to be remunerative on account of the large quantity of water to be evaporated. The following is the percentage composition of ordinary sea-water:—

	Per cent.
NaCl, ...	2·64
KCl, ...	0·07
$MgCl_2$, ...	0·31
$MgBr_2$, ...	0·01
$MgSO_4$, ...	0·20
$CaSO_4$, ...	0·13

The "salts gardens" on the shores of the Mediterranean consist of shallow pits into which sea-water is allowed to flow after it has been clarified by subsidence in a deep tank. The heat of the sun evaporates the water, and the crystals are raked out at intervals. The mother liquor ("bittern") contains magnesium salts, and is worked up for bromine and sometimes also for Glauber's salt ($Na_2SO_4.10H_2O$) (see *Minor Chemical Industries*, Vol. II., Chap. XVIII.) and occasionally for potassium chloride, though the latter industry has been nearly superseded by the production of potash salts at Stassfurt. In cold climates (as in Russia) advantage is taken of the fact that when a saline solution is exposed to a temperature below 0° C. = 32° F., nearly pure ice separates first. Sea-water is allowed to freeze in shallow pits, the ice is fished out and the freezing repeated; a mother liquor is ultimately obtained which will pay for evaporation.

In many countries salt for eating is taxed, but allowed free for industrial purposes, provided it be denatured so as to be unfit for human consumption. Thus in Germany, cattle salt is denatured with $\frac{1}{2}$ per cent. of ferric oxide and $\frac{1}{4}$ per cent. of wormwood; salt for manure with $\frac{1}{2}$ to 1 per cent. of soot or 2 per cent. of powdered lignite; salt for soda manufacture with sodium carbonate, sodium sulphate, sulphuric acid or ammonia; appropriate admixtures are used for other industries, the object in all cases being to render the salt not edible, while still fit for its particular industrial use.

Vitriol, the next raw material used in the manufacture of soda, has been dealt with already.

Calcium carbonate is used both as chalk and limestone, and any other available form—*e.g.*, recovered alkali waste (*v.i.*). The

limestone and chalk should be as free from silica as possible, and not dolomitic, the material containing the former impurity causing waste of soda as silicate, while dolomitic limestone contains magnesia, which is too feeble a base to do the work required of it. The calcium carbonate must be dried and crushed to fragments the size of a pea.

Small Coal.—The small coal, or "slack," used should be as free as possible from ash, which causes waste of soda by the silica it contains. Lump coal would be better, as containing a smaller proportion of ash, but it is too costly. Washed slack is poorer in ash, but often as much as 5 per cent. is commonly present; 8 per cent. of ash is still considered good by the alkali maker. The nitrogen in the coal causes waste of soda by the production of sodium cyanide. Wood charcoal—the best form of carbon for the process—is too dear for use now.

MANUFACTURE OF SALT-CAKE.—The reaction involved in the manufacture of salt-cake by the ordinary method is represented by the equation—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The apparatus in which the reaction is carried out is called the salt-cake furnace, and may have one of two forms. In either case

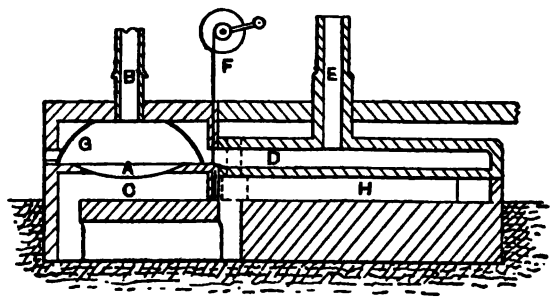


Fig. 4.—Salt-cake furnace.

A, Pan; G, cover; B, pan flue; D, muffle; E, muffle flue; C, furnace; H, flues; F, damper.

the first part of the decomposition, resulting in the formation of $NaHSO_4$ as well as Na_2SO_4, takes place in a circular or elliptical cast-iron pan, A (Fig. 4), varying in size from about 9 feet in diameter and 18 inches deep to 6 feet by 4 feet by 12 inches (in the case of one of elliptical shape). An arched cover, G, usually of acid-proof fireclay, suffices to collect the hydrochloric acid from the pan; the acid gas escapes by the fireclay flue, B. In order to complete the expulsion of hydrochloric acid, the contents of the pan is shifted into a fireclay muffle, D, also provided

with an exit flue, E, both pan and muffle being heated by the furnace, C, and the flues, H. To avoid any escape of gas from the muffle into the furnace flue, a higher pressure is maintained in the latter than that which prevails in the muffle, so that the leakage, if any, is in the other direction. In this country the muffle is frequently dispensed with, in which case the direct flame of the fire is allowed to play over the salt-cake spread on the hearth of a kind of reverberatory furnace, the hydrochloric acid escaping together with the furnace gases. Under these conditions the pan is heated by a separate furnace. The charge is about 6 to 16 cwts., the smaller quantity being used for furnaces without muffles (**open roasters**), which can be worked off in about one hour, and the larger for muffle furnaces (**close or blind roasters**), in which the time for each batch is about two hours. The acid used is generally of the strength of that coming from the Glover tower, having a specific gravity of 1·72. The weight required of acid of this strength is rather more than that of the salt charged. The action is at first violent, and as it slackens is aided by stirring; when the mass becomes pasty, the damper, F, is raised and the charge pushed over by a "shoving-rake" into the roaster, where its decomposition is completed at a bright red heat. The yield is 116 to 120 parts of salt-cake for 100 parts of salt charged.

Various mechanical furnaces for preparing salt-cake have been devised, but that originated by Mactear alone appears to be in use. It consists essentially of a circular firebrick hearth which rotates beneath a furnace dome that carries the exit flues. In the centre of the dome there is a hopper, through which salt and acid are fed into a central pot, which serves as the pan, the rest of the bed of the furnace acting as the roaster. The process is continuous, and the contents of the pot overflows on to the rotating bed, where the charge is gradually worked towards the circumference by fixed rakes, and, being heated by the flame of the furnace, is completely decomposed by the time it has reached the circumference, where it drops into an annular delivery trough, the salt-cake therein serving as a lute to the edge of the rotating bed. In this case the whole of the HCl is mixed with all the furnace gas.

Instead of using sulphuric acid to decompose salt, potential sulphuric acid—*i.e.*, SO_2, O and H_2O—can be employed, as in the Hargreaves and Robinson process. The reaction that occurs is—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$

In order that the reaction may be complete, the salt must be in a sufficiently porous state to allow the gases to penetrate it thoroughly, an object which is attained by moistening it, moulding it into cakes, and drying it. These cakes are charged into vertical cast-iron cylinders holding about 40 tons each, heated by external vertical flues. Gases from a pyrites burner are mixed with super-

heated steam, and caused to traverse the cylinders *seriatim*, entering at the top and passing out at the bottom. The passage of the gases is systematic—*i.e.*, the fresh gas always meets nearly converted salt, and exhausted gas passes away through fresh salt. The temperature at which the reaction obtains is about 500° C. = 932° F., and is partly maintained by the heat evolved in the course of the reaction, which is exothermic. The movement of the gas is produced by a Roots blower placed at the end of the cylinders, and likewise serving to pass the HCl on to the condensers.

Good commercial salt-cake will contain not less than 97 to 98 per cent. of Na_2SO_4. About two-thirds of the salt-cake made is used for the production of soda, for which purpose it should be as free as possible from chlorides. A large proportion of the remainder is employed in glass making, for which it is required free from iron, an object attained by dissolving it in water, making the solution alkaline with lime, whereby ferric hydroxide is precipitated, and recrystallising. As sodium sulphate normally crystallises as $Na_2SO_4,10H_2O$, the cost of freight is considerable, and it is, therefore, sometimes prepared as the anhydrous salt, the formation of which can be induced by adding various substances—*e.g.*, a crystal of Na_2SO_4 itself—to a solution of the salt at a temperature above 40° C. = 104° F.

Hydrochloric Acid.—In whatever way the conversion of sodium chloride into sulphate may have been effected, the gas HCl has to be condensed by absorption in water, save in the rare cases where it is used as such (Deacon's process, *q.v.*). This is the more important inasmuch as it is illegal to allow more than 0·2 grain of HCl per cubic foot of chimney gases to escape into the air. The gases from the pan are usually collected separately from those evolved in the roaster, being purer, and in cases where open roasters are used, more concentrated. In all cases the gases from the furnace are cooled by passing through a length of earthenware pipes or sandstone flues, or even through iron pipes, provided the temperature of these be not allowed to fall to the condensation point. An alternative plan of cooling consists in injecting a spray of water into stone tanks through which the gases pass, or the gases are led up a small tower fed with a limited amount of water, which suffices to cool the gas and condense sulphuric acid and stop flue dust (both the latter impurities being derived from the roaster). The gas is then passed through a series of stone tanks or, on the Continent, "bombonnes" (Woulfe's bottles) half filled with water, and exposing sufficient surface to the air to allow the HCl to be absorbed by the water. They are provided with side pipes, and are connected together so that a stream of HCl proceeds in one direction and is met by a flow of water in the opposite direction. The strongest acid is obtained in these condensers, but all the gas is not absorbed, so that it must finally be passed through a coke tower supplied with water. The tower is

built of acid-proof bricks and varies from 40 to 100 feet in height. The yield of acid is about 130 to 148 parts of aqueous acid of 1·17 to 1·18 specific gravity (containing 34 to 36 per cent. HCl) per 100 parts of salt-cake made.

By far the greater portion of this acid (**muriatic acid**) is used for making chlorine (Vol. II., p. 35), the remainder being employed in many minor industries. Crude muriatic acid contains as impurities ferric chloride and organic matter (which give it a yellow colour), arsenic and sulphuric acid. Arsenic is derived from the vitriol made from pyrites, which is commonly used. Most of the impurities in hydrochloric acid can be removed by distillation, except arsenic, which comes over with the first fraction as $AsCl_3$; the later portions may, however, be obtained free from this impurity. An alternative plan for removing the arsenic consists in precipitating it as As_2S_3 by means of H_2S, allowing the precipitate to settle, and distilling the acid.

MANUFACTURE OF BLACK ASH.—This is the next step in the process of making sodium carbonate by the Leblanc method. It is effected by heating a mixture of sodium sulphate (salt-cake) with calcium carbonate and small coal. The reaction may be assumed to take place in two stages—

$$(1)\ Na_2SO_4 + C_2 = Na_2S + 2CO_2.$$
$$(2)\ Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The resulting black ash is thus essentially a mixture of sodium carbonate and calcium sulphide. The sulphate should contain not more than 0·5 per cent. of NaCl nor more than 1·5 per cent. of free acid, calculated as SO_3. The proportions adopted in practice are—100 parts of salt-cake, 100 of limestone or dry chalk, of the size of a pea, and 40 to 60 parts of coal. The proportion of calcium carbonate and coal is greater than is indicated by the above equations, because, inasmuch as black ash is only clinkered and not fused, an excess of these reagents must be present to ensure each particle of salt-cake coming into contact with them. The excess is also useful as promoting the porosity of the black ash and favouring lixiviation, and, further, by generating CO in the interior of the mass when this is plastic at the last stage of the process, thus—$CaCO_3 + C = CaO + 2CO$. The CO renders the black ash porous like dough, and the subsequent hydration of the lime, simultaneously produced, disintegrates the masses of black ash during lixiviation. The operation is conducted in a species of reverberatory furnace, closely resembling the roaster of the salt-cake furnace, but with a hearth in place of the muffle. The half of the hearth nearer the grate is about 3 inches lower than that near the flue; the charge is introduced through a hopper on to the upper or back half, where it is dried and subjected to a preliminary heating, after which it is raked over to the lower part of the hearth, which has a temperature

of from 700° to 1,000° C. = 1,292° to 1,832° F. Here the charge is heated until the sodium sulphide, which at first forms (*v.s.*), is fused, and the mass becomes a thick paste, which is then thoroughly mixed by means of a rake and gradually drawn towards the door of the furnace, situated at the side of the lower hearth. There is a copious evolution of CO_2, and the mass becomes more pasty; the reaction evolving CO (*v.s.*) now sets in, this stage being recognised by the bursting of small jets of burning CO from the charge. The mass is then raked into a "ball" and withdrawn into an iron truck, where its quality can be judged by the continued evolution of CO and the expansion of the ball. It is usual to utilise the waste heat from the black-ash furnace to concentrate the liquor obtained by lixiviating the black ash; for this purpose a boiler pan is placed in a prolongation of the flue, so that the hot products of combustion pass over the surface of the liquor.

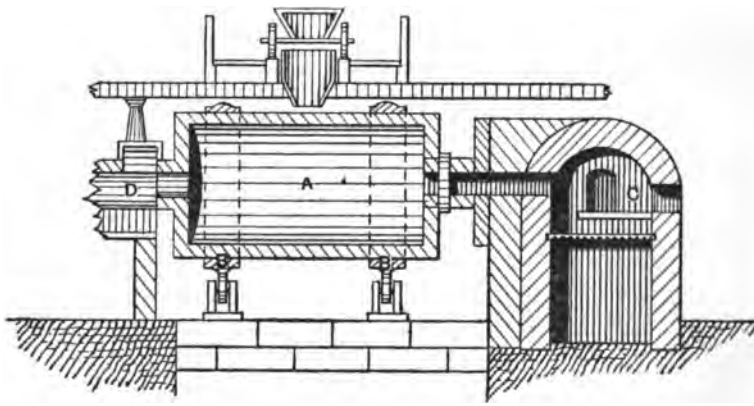


Fig. 5.—Revolving black-ash furnace.

A, Cylinder; B, B, rings; C, furnace; D, flue.

Mechanical furnaces for the production of black ash are known as **revolvers**. Inasmuch as the chief function of the workman in making black ash consists in turning and mixing the charge, it is obvious that if this mixing be effected mechanically, larger charges can be handled in a given time, and better intermixture can be secured. An ordinary revolving black-ash furnace consists of a cylinder, A (Fig. 5), made of boiler plate and lined with firebrick, resting on rollers on which work rings, B, B, concentric with the cylinder. The central part of each end of the cylinder is open, and is so placed that the hot gases from the furnace, C, can pass through it, supplying the heat necessary to convert the charge, and escaping by the flue, D, in which boiling-down pans may be set. Usually, ordinary large furnace grates

are used as the source of heat, but a producer would probably be better. The charge is introduced and removed through a manhole in the side of the cylinder. The revolver is driven by suitable gearing so that it can be rotated slowly at the beginning of the process (1 revolution in four minutes) and afterwards at a quicker rate (5 revolutions per minute). The charge is much larger than with the roaster furnaces, and need not be mixed before it is introduced, mixture being effected by the rotation of the cylinder, aided by the agitation produced by two fixed projections on the lining, called "breakers." The calcium carbonate and two-thirds of the coal are first put in and the cylinder revolved until some caustic lime has been formed; the salt-cake and the remaining coal are then added, and the revolution continued at a higher speed until the operation is complete. The object of this preliminary "liming" is to ensure the presence of enough caustic lime in the black ash to allow of its easy lixiviation.

Properly made black ash has a blackish-brown surface with a grey porous fracture; its composition may be gathered from the following analysis (*Kolb*):—

Sodium carbonate,	44·79	per cent.
,, silicate,	1·52	,,
,, aluminate,	1·44	,,
,, sulphate,	0·92	,,
,, chloride,	1·85	,,
Calcium oxide,	9·68	,,
,, sulphide,	29·96	,,
,, carbonate,	5·92	,,
Ferric oxide,	1·21	,,
Coal,	1·20	,,
	98·49	,,

Traces of cyanide, ferrocyanide, soda in an insoluble form, and Na_2S are also generally present.

Black ash absorbs moisture and CO_2 from the air, the lime being thus slaked, causing the disintegration of the mass; long exposure is undesirable, lest a reverse reaction between the CaS and Na_2CO_3 occur, involving waste.

Lixiviation of Black Ash.—Well-made black ash is sufficiently porous to be easily extracted even when in comparatively large pieces, but if ill-made, and therefore dense, it must be crushed to a coarse powder before lixiviation. The method of extraction consists in exposing the fragments in tanks, provided with false bottoms, to systematic treatment with water, in such a way that fresh water comes in contact with nearly exhausted ash and strong liquors with fresh ash. Contact of the ash with air is avoided as much as possible, as a rapid oxidation of calcium sulphide, and consequent loss of soda by double decomposition

of the calcium sulphate thus formed with the sodium carbonate, occurs. Inasmuch as the black ash is anhydrous, and contains a considerable quantity of caustic lime, it causes a rise of temperature when first brought into contact with water; thus the temperature of the strong liquor may be 60° C. = 140° F., while that of the weak liquor should not exceed 37° C. = 99° F., as otherwise the reverse reaction between CaS and Na_2CO_3 tends to take place; for the same reason the liquor must not be allowed to become stronger than is indicated by a specific gravity of 1·28. Besides being inevitably associated with loss of soda, Na_2S, the product of the reverse reaction, is objectionable on account of its solvent action on FeS (derived from the iron of the tank), which colours the liquor green. The calcium sulphide and other insoluble substances left in the tank are periodically removed, and constitute **tank waste** (*q.v.*). The constitution of the **tank liquor** obtained in this way is given below:—

Na_2CO_3 + NaOH, ...	23·60 per cent.
NaCl, ...	0·50 ,,
Na_2S, ...	0·13 ,,
$Na_2S_2O_3$, ...	0·30 ,,
Na_2SO_4, ...	0·23 ,,
	24·76 ,,

Small quantities of sodium sulphite, cyanide, ferrocyanide, thiocyanate and silicate, and ferrous sulphide are also present. As much as 20 per cent. of the alkali will generally be in the form of caustic soda, which results from the action on the sodium carbonate of the surplus lime, used in the black ash process for indirectly imparting porosity as described above. The tank liquor is allowed to settle, and when clear is submitted to the action of CO_2 (in order to carbonate the caustic soda) by being run down a tower filled with broken stoneware, or, preferably, containing chains or wire rope, down which the liquor trickles; lime-kiln gases are passed up the tower. During the carbonation, sodium sulphide, as well as the hydrate, is converted into carbonate, and ferrous sulphide is thrown out of solution; at the same time sodium silicate and aluminate are decomposed, the acid radicles being precipitated and the quantity of useful soda, Na_2CO_3, increased. Sodium ferrocyanide is an objectionable impurity in tank liquor, inasmuch as it appears in the calcined soda ash as Fe_2O_3 and impairs its colour. It can be removed by heating the tank liquor to 180° C. = 356° F. under pressure, when it reacts with another impurity, sodium thiosulphate, to form sodium thiocyanate and sulphite, the iron being separated as ferrous oxide; it may also be removed by precipitation with a zinc salt as zinc ferrocyanide.

Evaporation of Tank Liquor for Soda Ash (Anhydrous

Na_2CO_3).—The clear settled tank liquor, carbonated and freed from ferrocyanide, is evaporated, at near its boiling point, for the production of **black salt**, impure $Na_2CO_3.H_2O$. The evaporation may be performed, as already mentioned, by the waste heat of the black-ash furnaces, but the product is then contaminated by flue dust and SO_2 from the fuel. Pans heated from the bottom, and mechanical evaporators, such as Thélen's, in which the salt is mechanically scraped out as fast as formed, are also used. The black salt is drained from the mother liquor (**red liquor**), which is boiled down separately for a less pure alkali, or is converted into caustic soda (*v.i.*). Evaporation by multiple effect under diminished pressure (see *Sugar*, Vol. II., Chap. VIII.) has not proved successful.

Finishing the Soda Ash.—To drive off the molecule of H_2O in the black salt, calcination at a red heat in an ordinary reverberatory furnace is necessary. When carbonation of the tank liquor has been omitted, the black salt is mixed with sawdust before calcination, in order that the combustion of this may supply CO_2 for the conversion of NaOH and Na_2S into Na_2CO_3; the product is, at best, less pure than that from carbonated tank liquor. Various mechanical carbonating furnaces have been devised, the chief advantage of which lies rather in the saving of labour than of fuel.

The best commercial soda ash is white, and contains not more than a trace of caustic soda and 98 to 99 per cent. of Na_2CO_3. That carbonated with sawdust still contains at least 2 per cent. of caustic soda, and has to be refined by dissolution in water, removing Fe_2O_3 by settlement and re-evaporation in pans heated by coke fires, followed by calcination. The product is known as **refined alkali**. For purposes, such as soap making, where caustic soda is prepared from soda ash, a grade known as "caustic ash," containing as much as 20 per cent. of caustic soda, is used. **Soda crystals**, $Na_2CO_3,10H_2O$ (**washing soda**), though containing only 37 per cent. of Na_2CO_3, is preferred for scouring wool and for domestic use, largely because of its freedom from caustic soda. It is usually prepared by recrystallising the solution of soda ash, which should be freed from sulphide and should contain not more than 2 per cent. of caustic soda. The solution for crystallisation is made with water above 34° C. = 93° F. (the temperature at which $Na_2CO_3,10H_2O$ is most soluble), and is saturated; it is allowed to cool in shallow crystallising pans. The formation of good crystals is said to be promoted by the presence of 1 per cent. of sodium sulphate. The mother liquors are boiled down and calcined.

Crystal carbonate, $Na_2CO_3.H_2O$ (83 per cent. of Na_2CO_3), is a proprietary name given to the product obtained by crystallising from a boiling saturated solution of carbonated and thoroughly purified tank liquor. It is applicable to the same purposes as

those for which soda crystals are used, and costs less for transport per unit of Na_2CO_3.

Bicarbonate of Soda, $NaHCO_3$.—This is prepared by carbonating the normal carbonate with any concentrated form of CO_2. Volcanic gases and CO_2 from fermentation are used, otherwise CO_2 evolved by the action of HCl on limestone is employed. Soda crystals, as such, are generally used as the raw material, though a saturated solution of soda ash may be substituted. (Bicarbonate is now chiefly made by the ammonia-soda process —*q.v.* Vol. II., p. 43.) In the former case the crystals, placed on a drainer, are exposed to the action of the gas for six to nine days; much water comes away, in accordance with the equation—

$$Na_2CO_3.10H_2O + CO_2 = 2NaHCO_3 + 9H_2O.$$

This forms a liquor which is boiled down and yields an impure weak soda ash. In the second case the bicarbonate separates from the solution. Drying at a temperature not exceeding 45° C. = 113° F. is necessary to avoid loss of CO_2. **Sodium sesquicarbonate,** $Na_2CO_3.NaHCO_3.2H_2O$, is also prepared from mixed solutions of sodium carbonate and bicarbonate, crystallised not below 35° C. = 95° F.; it is used for wool washing. Sodium bicarbonate is a milder alkali than the normal carbonate, and on this account is used when the action of the latter is too drastic.

Caustic Soda.—The reaction involved in the production of caustic soda (NaOH) from sodium carbonate is expressed by the equation—

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

In practice, caustic soda is prepared by causticising purified tank liquor; this must be well settled, and have a specific gravity of 1·08 to 1·10. The purification of the tank liquor by exposure to CO_2 is omitted in the case of that which is to be causticised, inasmuch as a portion of the soda is already present as caustic soda, and the carbonation of this would involve waste of lime in subsequently decarbonating. The tank liquor must, however, be freed from sulphide; this is effected either by blowing in air, the oxidising action of which may be enhanced by the addition of Weldon mud (*v.i.*), or by precipitating the sulphide as ZnS or PbS, which process is preferable for high-grade (77 per cent.) caustic. The strength of the liquor to be causticised is limited to that corresponding with a specific gravity of 1·10, because stronger liquors prevent the completion of the reaction, inasmuch as strong caustic soda is capable of removing CO_2 from $CaCO_3$, the above equation becoming reversed. In order further to prevent this back action, the proportion of lime employed is in excess of that indicated by the equation, advantage being thus taken of the principle of mass action.

The process consists in placing slaked lime (11 cwts. to 1 ton of caustic lime per 10 tons of tank liquor) in an iron cage and

immersing it in the boiling tank liquor, purified, and of the concentration indicated above. The liquor is kept agitated by steam injection or by paddles. When the liquor is completely causticised the clear solution is drawn off. It has approximately the following composition:—

$NaOH$, ...	10·25 per cent.
Na_2CO_3, ...	3·29 ,,
$NaCl$, ...	0·14 ,,
$Na_2S_2O_3$, ...	0·29 ,,
Na_2SO_4, ...	0·25 ,,

The calcium carbonate sludge, left at the bottom of the causticising pan, is filtered and washed, and the washings used for diluting the tank liquor for the next causticisation. The washed lime mud will serve, instead of bought calcium carbonate, for preparing a further quantity of black ash.

Red liquor, the mother liquor from black salts (*v.s.*) was originally largely used for the production of caustic soda as already containing much caustic. The product is less pure than that from tank liquor. It sufficed to boil down this red liquor, when the sodium carbonate and other salts contained in it separated and left an impure concentrated caustic liquor.

The production of solid caustic soda from the causticised liquor takes place in two stages. The liquor is boiled down in pans to specific gravity 1·4 and the sodium carbonate and other salts are fished out; the liquor is settled and the evaporation completed in caustic pots. The salts separated during concentration are worked up with a fresh batch of black ash. Towards the end of the concentration in caustic pots, any residual sulphide is oxidised by the addition of about 1 per cent. of sodium nitrate. This converts the sulphide into sulphate, and is at the same time reduced to nitrite, which remains in the caustic. The material in the pot is allowed to settle, and ladled out into drums, in which it solidifies. Various grades of caustic soda are made, known commercially as "60 per cent.," "70 per cent.," "77 per cent." (Na_2O) (*v.i.*) and "caustic bottoms." These contain respectively about 80 per cent., 90 per cent., 96 per cent., and 59 per cent. of NaOH, the remaining salts present being chiefly sodium chloride and sodium sulphate, save in the case of bottoms, when as much as 20 per cent. of insoluble matter may be present. Caustic soda is largely used by soap and paper makers, and in the purification of petroleum and tar oils; there are various minor applications of this alkali.

Commercial standards for Trading in Alkali.—The only rational way of stating the strength of soda ash and caustic is in terms of the percentage of Na_2CO_3 and NaOH, respectively. This method is not generally adopted.

The German plan for both substances consists in reckoning

the total alkali as Na_2CO_3, a process indefensible for caustic soda. In this country the total alkalinity is stated in percentage of Na_2O, each per cent. being 1°; this would be a suitable method but for the custom of taking the atomic weight of sodium as 24, which causes the stated percentage to be higher than the real. Nowadays the valuation is made correctly and translated by various fraudulent methods of calculation into a higher alleged content of soda, the method varying with the district. Stated by the English method (Na = 24) pure sodium carbonate is 59·26° strength, the real value (Na = 23) being 58·49°. Pure caustic soda on the same standard is 78·05°, the real value (Na = 23) being 77·5°

TREATMENT OF TANK WASTE (ALKALI WASTE).—It will be realised from the foregoing, that practically the whole of the sulphur of the sulphuric acid used in the manufacture of salt-cake remains in the tank waste from the extraction of black ash. The dry waste thus produced amounts to 1½ tons per ton of soda ash made. Formerly the whole of this had either to be heaped outside the works, or carted out to sea, if the nuisance, arising from the sulphuretted hydrogen evolved from it, became intolerable. Its composition is given below:—

Na_2CO_3,	1·63	per cent.
$CaCO_3$,	38·81	,,
$Ca(OH)_2$,	9·53	,,
CaS,	35·12	,,
CaS_2O_3,	1·49	,,
Coal,	6·27	,,
Al_2O_3,	0·13	,,
FeS,	2·76	,,
SiO_2,	1·21	,,
Sand,	2·61	,,
	99·56	,,

The action of air and moisture on this substance produces hydrosulphides, polysulphides, sulphites, and thiosulphates. These being washed out by the rain, drain away from the heap, the drainage giving up H_2S by the further action of CO_2 of the air, and also itself contaminating adjacent water supplies.

Inasmuch as sulphur is, with the exception of nitrate, the most expensive raw material used in the production of soda, the only rational way of dealing with alkali waste consists in recovering the sulphur as such. The sole method successfully effecting this is the Chance-Claus recovery process, which is worked as follows:—Fresh alkali waste is made into a cream with water and subjected to the action of lime-kiln gases in a set of vertical cylinders, 16 feet by 5 feet. The CO_2 of the lime-kiln gases first attacks CaS of the alkali waste, producing $CaCO_3$ and H_2S: $CaS + H_2O + CO_2 = CaCO_3 + H_2S$. The H_2S passes into the

next cylinder containing alkali waste and is absorbed, forming calcium hydrosulphide $Ca(SH)_2$, approximately pure nitrogen, from the lime-kiln gases, escaping. After the waste has been completely decomposed in the first cylinder, CO_2 will pass on to the next and react with $Ca(SH)_2$, thus—

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S.$$

The sulphuretted hydrogen is collected in a gasholder. It will be seen that the rationale of the process consists in obtaining a fairly concentrated sulphuretted hydrogen by first enriching a portion of the waste to be treated and then decomposing this enriched waste. In practice, a set of seven decomposing cylinders is found requisite for this purpose. The average strength of the sulphuretted hydrogen produced is 32 per cent. of H_2S, the remainder being nitrogen with a little CO_2. The residue from the tank waste, thus treated, consists of $CaCO_3$, containing a little alkali, and may be used for making black ash, and has been tried for the manufacture of Portland cement (*q.v.*), but is not well fitted for this purpose on account of the sulphur which it contains.*

The sulphuretted hydrogen stored from this process may be burnt, instead of pyrites, for vitriol making, but this method of utilisation is not remunerative; it is, therefore, used to produce recovered sulphur in a Claus kiln. The Claus kiln, which serves for the recovery of sulphur from H_2S however obtained (see *Gas Manufacture*, Vol. II., p. 76), is an apparatus devised for the smooth carrying-out of the reaction $H_2S + O = H_2O + S$, when the sulphuretted hydrogen is diluted with inert gas, such as nitrogen. The kiln consists of an iron cylinder, A (Fig. 6), lined with firebrick, and having a grate, B, at its lower part, upon which a layer of ferric oxide, C, about 18 inches thick, rests.

The dilute sulphuretted hydrogen constituting the Chance gases is mixed with about four-fifths of its volume of air, and the mixture is passed into the kiln below the grate. The ferric oxide which has already been heated is now kept hot by the heat of the combustion of the hydrogen in the H_2S, the combustion being induced by the presence of this hot oxide. The resulting steam and sulphur vapour pass into a series of chambers, in the first of which, D, the temperature is sufficiently high for liquid sulphur to be deposited, while in the succeeding chambers, E, flowers of sulphur are condensed. The combustion of the H_2S is not

* Another method of utilising tank waste is the Parnell and Simpson process, in which the waste liquors of the ammonia-soda process (*v.i.*) are worked up. The reactions involved are—

(1) $2NH_4Cl + CaS = CaCl_2 + (NH_4)_2S$.
(2) $(NH_4)_2S + 2CO_2 + 2H_2O = 2NH_4HCO_3 + H_2S$.

The H_2S is collected in a gasholder, and the ammonium bicarbonate used for making ammonia-soda.

generally complete in the Claus kiln, so that the exit gases must be passed through a furnace and washed, to avoid nuisance.

The Chance process for recovering sulphur from alkali waste is rapidly displacing other processes for effecting a similar object. The only one of these which needs notice here is that of Mactear

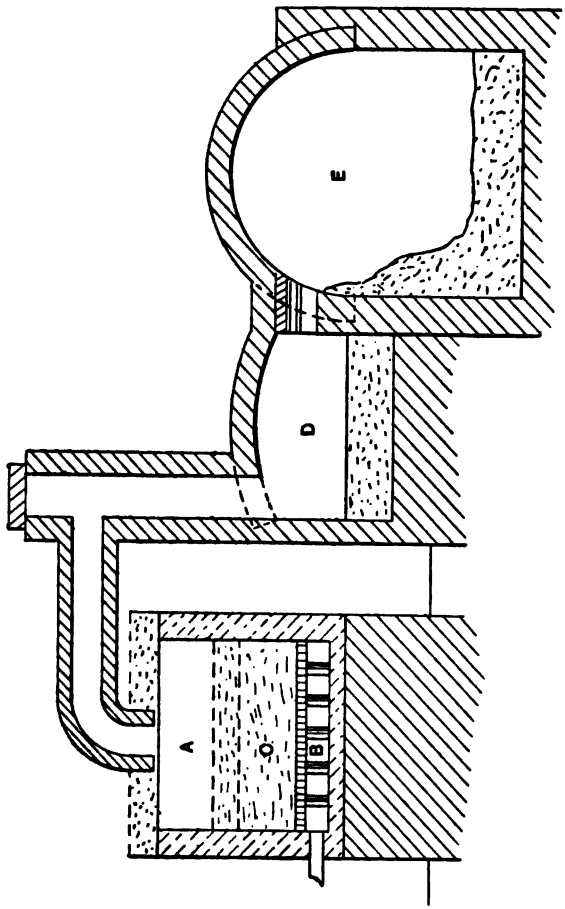


Fig. 6.—Claus kiln.

A, Cylinder; B, grate; C, layer of ferric oxide; D, E, chambers.

modified by Péchiney, which is designed for treating drainage from tank-waste heaps, thus avoiding the worst nuisance. Air is blown through the drainage until sufficient of the sulphide which it contains has been oxidised to thiosulphate, so that it reacts completely with the remaining sulphide when hydrochloric acid is added, according to the equations—

(1) $CaS_2O_3 + 2HCl = CaCl_2 + H_2O + SO_2 + S$.
(2) $Ca(SH)_2 + 2HCl = CaCl_2 + 2H_2S$.
(3) $SO_2 + 2H_2S = S_3 + 2H_2O$.

The sulphur is thus recovered.

CHLORINE AND BLEACHING POWDER.—The manufacture of chlorine for conversion into bleaching powder is always a part of the Leblanc process, because nearly all the chlorine of the salt appears as hydrochloric acid, which has fewer applications than has chloride of lime.

In order to prepare chlorine from hydrochloric acid, the hydrogen of the latter must be oxidised to water. While many oxidising agents will effect this, the cheapest is manganese dioxide, which reacts as follows:—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O\,;\; MnCl_4 = MnCl_2 + Cl_2.$$

Manganese tetrachloride ($MnCl_4$) exists in the brown solution of manganese dioxide in cold strong HCl. It is very unstable, and splits up on warming into manganous chloride ($MnCl_2$) and free chlorine. For manufacturing purposes, where the liquor is heated, the reaction may be considered to proceed thus—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

Such other oxidising agents as may be practically substituted for manganese dioxide will be dealt with later.

The hydrochloric acid, condensed as described above (p. 24), is used for making chlorine; it should contain at least 20 per cent. HCl (specific gravity 1·10), and is better when stronger; it should be as free as possible from sulphuric acid, for removing which in the form of barium sulphate, barium chloride has been used.

The manganese dioxide is always originally used as a manganese ore (an impure natural manganese dioxide), though nearly all of it is recovered as an artificial oxide (*v.i.*) after each distillation of chlorine, and used repeatedly. The manganese ore now comes chiefly from Huelva, and should contain at least 65 per cent. of MnO_2 and be free from calcium carbonate, because this wastes acid and yields CO_2, which contaminates the chlorine. The technical valuation of "manganese" for chlorine making consists in estimating the "available oxygen"—that is, the percentage of oxygen in the ore above that necessary to form the base MnO, and therefore available for oxidation of HCl.

Chlorine stills are stoneware, carboy-shaped vessels, filled with an inner perforated cylinder holding the manganese, and provided with an inlet neck for the acid and an outlet pipe for the chlorine; the still is heated by a steam jacket.

Another form consists of a stoneware cylinder with a false bottom for holding the manganese, covered by a leaden bell, the

lower edge of which is trapped by water in an outer vessel, which also serves as a water jacket for heating the still. Both the above forms are fit only for small installations.

In large works the stills are made on the pattern shown in Fig. 7; they consist of siliceous stone slabs, tongued and grooved, and made tight by caoutchouc or a lute of tar and fireclay. The walls are held in their place by iron clamps. A sandstone slab fitted in the same manner serves as a lid, and is provided with a manhole for charging the still, while a discharging hole is situated in one of the side slabs. The manganese rests on a

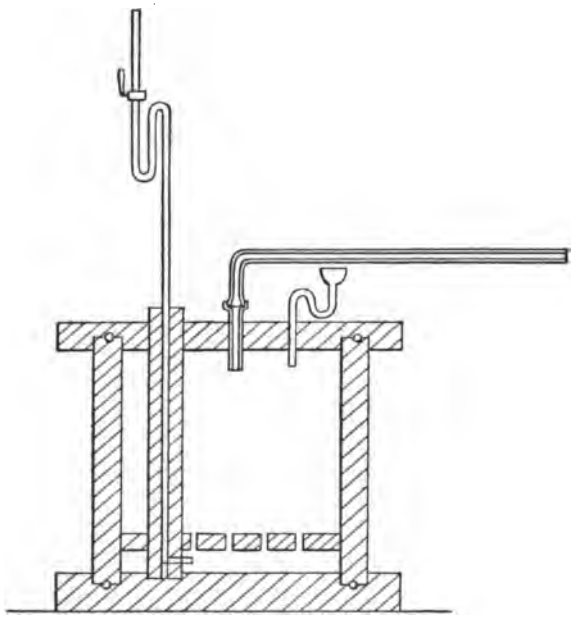


Fig. 7.—Chlorine still.

false bottom, to prevent caking; the charge is 6 to 10 cwts. The acid (25 to 35 cwts.) is run in through a lead pipe which terminates in an acid seal, and steam is supplied through another lead pipe, continued within the still as a stoneware column, which passes below the false bottom, where it has several openings for the distribution of the steam. The acid is run in quickly at first, chlorine being spontaneously evolved, and more acid added from time to time, until the evolution of chlorine slackens, when steam is slowly injected, the temperature of the still reaching 90° C. = 194° F. as a maximum. The charge is worked off in 24 to 48 hours. The chlorine, which escapes

through a leaden pipe in the lid, is passed into the bleaching-powder chambers, described below.

Even should the reaction between MnO_2 and HCl for the production of chlorine, given above, be capable of realisation in practice, half of the chlorine of the hydrochloric acid would be retained in the still as manganous chloride. On account of the presence in native manganese of other oxides than that of manganese, and of the impossibility of pushing the saturation of the hydrochloric acid to the point of neutrality, considerably more than half the acid is wasted, as far as the production of chlorine is concerned. Thus of the total hydrochloric acid used, it generally happens that one-third appears as chlorine, rather more than one-third as manganous chloride, and nearly the whole of the remainder as free hydrochloric acid, a comparatively small proportion being accounted for as ferric chloride, aluminium chloride, barium chloride, &c.

The comparative costliness of manganese has made its recovery, in order that it may again serve as an oxygen carrier, essential. The only method which successfully attains this object is the Weldon recovery process. The still liquor, consisting of manganous chloride, acid with hydrochloric acid, and containing some ferric chloride, is agitated in "neutralising wells" with ground chalk or limestone; here the free acid is neutralised, calcium chloride being formed, and the iron is precipitated as ferric hydroxide, the manganous chloride not being precipitated by this reagent except so far as the still liquor contains free chlorine (always the case), which causes a precipitation of an equivalent quantity of manganese as dioxide. The neutralised liquor is pumped into settlers of wrought or cast iron, and, after settling, is run off into iron cylinders, the "oxidisers"; the mud is washed, and the washings used for making milk of lime for the next operation. This consists in adding milk of lime in the proportion of 1 molecule of lime to 2 molecules of manganous oxide, the quantity generally amounting to 12 to 14 cwts. of lime per ton of bleaching powder made.* The lime must be free from magnesia, inasmuch as this is too feeble a base to decompose manganous chloride with the requisite rapidity, and, therefore, remains in the mud as MgO, ready to consume a portion of the hydrochloric acid in the mud-still. The oxidisers are placed vertically, and are supplied with air, and are fitted with a steampipe which maintains the temperature at 55° C. = 131° F. The reaction taking place in the oxidisers consists first in the precipitation of manganous oxide, and the formation of calcium chloride, by the action of the lime on the manganous chloride. This is oxidised by the stream of air with the formation, in the presence of lime, of calcium manganite ($CaO.MnO_2$) and manganous manganite ($MnO.MnO_2$).

* It is convenient, on account of commercial considerations, to calculate items of cost per unit of the finished product.

For further elucidation of the chemistry of this process it may be stated that when air is blown through a precipitate of manganous oxide, manganous manganite is formed, the oxidation only proceeding sufficiently far to provide an acid oxide (MnO_2) to combine with the basic oxide (MnO). The rapidity of absorption of oxygen is enhanced by the presence of a more powerful base than MnO—*e.g.*, CaO—when calcium manganite is formed; but it is impracticable to produce a calcium manganite in this way, unmixed with manganous manganite. It will be seen from what has been said, that the oxidised liquor consists of a solution of calcium chloride containing in suspension calcium manganite and manganous manganite; the proportions of the lime, and of manganese as manganous oxide and manganese dioxide, being in accordance with the following analysis:—

MnO_2, ...	66 per cent.
MnO, ...	17 ,,
CaO, ...	16 ,,
	99

The necessity for the use of lime has been indicated above; its quantity is reduced as far as possible in order to avoid a greater loss of acid in the still than is absolutely necessary, by adding still liquor containing manganous chloride ("final liquor") to the mud after the first stage of blowing; a portion of the lime in the calcium manganite is thus removed, leaving a more acid calcium manganite, and forming calcium chloride and manganous hydroxide, the latter being then converted into manganous manganite by the further action of air. The calcium chloride in the liquor plays an important part in assisting the oxidation, by reason, it is believed, of its solvent action on calcium manganite, which appears to act as a carrier of oxygen. The precipitated manganites thrown down in the oxidisers are known as "Weldon mud." When the process is properly conducted, about 80 per cent. of the total manganese in the mud is in the form of MnO_2, so that its value for producing chlorine is equal to that of a high grade native manganese, and is enhanced by its finely-divided condition. The contents of the oxidisers are run into settlers, the calcium chloride solution is drawn off, and the Weldon mud, still fluid enough to pass through a pipe, transferred to the mud-stills, which are similar in design to those used for the native manganese, but larger, generally octagonal and not provided with a false bottom, because the mud is completely soluble in the hydrochloric acid. The waste liquor from the still is worked up again in the same way.

The recovery of manganese by Weldon's process is so complete that the amount of fresh manganese ore requisite to replace that lost, is about 1 per cent. of the bleaching powder made.

It will be seen that only one-third of the chlorine in the salt,

the original raw material, appears as gaseous chlorine, the remainder being run to waste as calcium chloride. The improvements which have been suggested in the preparation of chlorine by the use of manganese dioxide as an oxidising agent, have been in the direction of reducing this waste of two-thirds of the chlorine. In the most hopeful of these, magnesium carbonate is substituted for calcium carbonate for neutralising the still liquors, in order that advantage may be taken of the fact that magnesium chloride decomposes when heated with the evolution of a part of its chlorine as hydrochloric acid. The neutralised still liquor is evaporated to dryness, and the residue roasted in air, so that chlorine is evolved and magnesium manganite, which can be used as an oxidiser in the chlorine stills, remains. By this means a larger proportion of chlorine can be obtained, amounting to 60 per cent. or more of that in the salt. This process is not at present in extended use.

Numerous oxidising agents, other than MnO_2, have been suggested for the production of chlorine, but that which has alone proved moderately successful is atmospheric oxygen, employed as in the Deacon process. The principle of this process is expressed by the equation $2HCl + O = H_2O + Cl_2$, which can only be realised—and then partially—when both the HCl and H_2O are gaseous, as the decomposition of 2 mols. of HCl (gaseous) involves the absorption of 44 Cal., and the formation of 1 mol. of H_2O (gaseous) evolves 58·7 Cal.; this leaves a balance of 14·7 Cal., so that the reaction is exothermic, whereas, when both substances are liquid the reaction is endothermic, and, therefore, cannot take place spontaneously. The oxidation of HCl by atmospheric oxygen can be effected by supplying energy from without in the form of heat; but the process is slow and incomplete. In the presence of cupric chloride, however, the reaction takes place more readily, inasmuch as cupric chloride, by dint of its facility for dissociating into cuprous chloride and chlorine at 400° C. = 752° F., acts as a carrier of oxygen from the air to the hydrogen of the HCl. The stages of the reaction may be represented thus (according to Hurter):—

$$(1)\ 2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

The oxygen of the air then reacts with cuprous chloride thus—

$$(2)\ Cu_2Cl_2 + O_2 = 2CuO + Cl_2.$$

The cupric oxide is regenerated to cupric chloride by the action of the HCl—

$$(3)\ CuO + 2HCl = CuCl_2 + H_2O.$$

The same cycle of changes is then repeated.

In practice, the gaseous HCl from the decomposing pans of salt-cake furnaces (that from the roasters is too dilute) is cooled

by passage through long pipes and a scrubber, and thus freed from the bulk of the steam which accompanies it; it is then heated by traversing a stove similar to those used for hot-blast furnaces (Vol. I., p. 131) to a temperature of 500° C. = 932° F. The acid gas is pulled through the whole apparatus by a Roots blower at the exit end, enough air being drawn in through the doors and flues of the furnace which heats the decomposing pan. About 4 vols. of air to 1 vol. of HCl are required. This mixture of gases, having passed through the stove already referred to, enters the decomposer, which consists of a vertical cast-iron cylinder, shown in horizontal section in Fig. 8. The mixture of gases passes into the outer annular space, A, then through the annular layer of active material, B, and escapes into the cylindrical centre space, C, whence it is drawn off by a pipe, D.

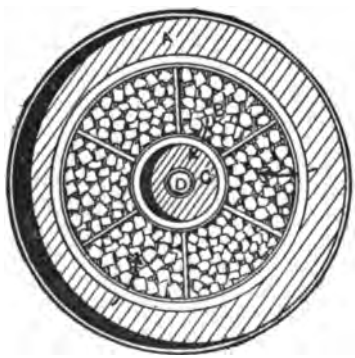


Fig. 8.—Decomposer for Deacon's chlorine process.

A, Annular space; B, active material; C, centre space; D, pipe.

The active material consists of burnt clay broken into lumps and saturated with a solution of cupric chloride, the mass containing 0·6 to 0·7 per cent. of copper. After having been used for a time, corresponding with an output of 10 to 12 cwts. of bleaching powder, the material ceases to be active and must be renewed. The decomposer is not externally heated, the temperature of the incoming gases sufficing to carry on the reaction. The exit gases from the decomposer contain from one-half to one-third of the chlorine which is present, in the free state, the remainder being still as HCl, which is condensed in the usual way. If the gas is to be used for making bleaching powder, it is dried by passing up a tower fed with vitriol. When properly worked the process yields a gas containing as much as 10 per cent. of chlorine, but this strength is much below that of the gas obtained from manganese stills, and on account of this comparative dilution the bleaching-powder chambers in which it is absorbed differ in detail from those described below for stronger chlorine.

Production of Bleaching Powder.—The process for manufacturing bleaching powder, or **chloride of lime**, consists in passing chlorine over slaked lime, which absorbs the gas, forming "chloride of lime." The reaction which occurs is still a subject

of discussion, but, whatever its course, it appears to result in the production of a compound CaCl.OCl, which, on contact with water, decomposes according to the equation—

$$2(CaCl.OCl) = Ca(OCl)_2 + CaCl_2.$$

The calcium hypochlorite [$Ca(OCl)_2$] and chloride ($CaCl_2$), formed in this way, dissolve in the water, leaving a residue of unaltered slaked lime.

The slaked lime must be prepared from "fat" quicklime by sprinkling with water, in order that no excess of the latter may be present, and must be sifted from unslaked lumps. It is spread on shelves in large leaden chambers, about 100 feet long, 7 feet high, and 10 to 20 feet in width, the floor being made of stone slabs. The chlorine is admitted into these systematically, and the progress of absorption is judged by the colour of the gas as observed through windows in the walls. When the yellow colour has disappeared, the lime is turned over by spades and fresh chlorine is admitted, after the absorption of which the process is complete. When the chambers are not worked in sets, the excess of chlorine is drawn off and absorbed in milk of lime, to make bleach liquor. The bleach maker is not allowed to let gases containing more than 2½ grains of chlorine per cubic foot escape into the air. When dilute chlorine, such as is obtained in the Deacon process, is used, systematic working is a necessity, and the chambers are much larger than usual.

The average yield of bleach is about one and a-half times the weight of the slaked lime used. When properly made, it is a nearly pure white powder, which becomes slightly damp when exposed to air, and decomposes in the presence of moisture and CO_2, which cause it to give off hypochlorous acid; it is the presence of this body which gives chloride of lime its characteristic smell. It should contain at least 35 per cent. of "available chlorine"—*i.e.*, chlorine in a condition to effect oxidation, and, therefore, bleaching action.

Where a local market exists for bleach, "bleach liquor" is sometimes prepared by passing chlorine into milk of lime, containing 1 to 1½ lbs. of slaked lime per gallon of water, and mechanically agitated. It contains calcium hypochlorite and calcium chloride, and the available chlorine, per unit of lime, is higher than in bleaching powder, because lime is more thoroughly attacked when in an emulsion than when in the solid state. The *eau de Javelle* and *eau de Labarraque* first made in France are "chloride of potash" and soda respectively, and are prepared by passing chlorine into solutions of the corresponding carbonates, whereby the chlorides and hypochlorous acid are produced—

$$Na_2CO_3 + 4Cl + H_2O = 2NaCl + CO_2 + 2HOCl.$$

They contain more available chlorine than bleach, but are less stable. Liquid chlorine, contained in steel cylinders at a pressure of 8 atmospheres, is now a commercial product. It boils at $-33{\cdot}6°$ C. $= -28°$ F., and its specific gravity is 1·33.

Potassium Chlorate.—This salt is also a bye-product of the manufacture of alkali by the Leblanc process, free chlorine being essential for its production. While hypochlorites are formed when chlorine is passed into cold alkaline liquids, chlorates are produced when the temperature is near 100° C. = 212° F. In the manufacture of potassium chlorate, calcium chlorate is first prepared, thus—

$$6Ca(OH)_2 + Cl_{12} = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

This is decomposed by the addition of potassium chloride, thus—

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

It is cheaper to form calcium chlorate as an intermediate product, because five-sixths of the potash in caustic potash, if that were used directly, would be converted into chloride, a comparatively low-priced salt.

The first stage in the process consists in passing chlorine into cast-iron cylinders containing milk of lime and provided with agitators, several such vessels being worked systematically. The heat evolved during the reaction raises the temperature sufficiently to induce the production of calcium chlorate instead of calcium hypochlorite. Even in careful work a certain amount of oxygen is evolved from the decomposition of calcium hypochlorite, representing a corresponding loss of chlorate, this loss being smaller when an excess of chlorine is present. The finished liquor, which is pink from the presence of calcium permanganate, is run into settlers, and potassium chloride is added. The clear liquor, containing potassium chlorate and calcium chloride, is run off, and the mud, containing impurities in the slaked lime, is washed, the washings being used in making the next batch of milk of lime. The chlorate liquor is boiled down in iron pans until its specific gravity is 1·35, when potassium chlorate crystallises; the salt is recrystallised before it is marketed. The mother liquor contains at least 12 per cent. of the total chlorate, part of which may be recovered by cooling the liquor to $-20°$ C. $= -4°$ F., when more potassium chlorate crystallises. It is economical of chlorate to substitute magnesia for lime, as a portion of the magnesium chloride produced can be crystallised before adding the potassium chloride, and the final mother liquors are less bulky and hold less potassium chlorate in solution.

Potassium chlorate is anhydrous, and is used in the manufacture of matches, fireworks and explosives, and generally as an oxidant. Sodium chlorate, which is preferable for some purposes to potassium chlorate, on account of its greater solubility, is

made by removing a part of the calcium chloride from calcium chlorate liquor at a temperature of 10° to 12° C. = 50° to 54° F., and adding sodium sulphate; the precipitated calcium sulphate is filtered off, and the solution of sodium chlorate is evaporated to crystallisation. The salt is anhydrous.

II. THE AMMONIA-SODA PROCESS.

This process—which was first put into practical shape by Solvay (1863), although the knowledge of its fundamental reaction is of much older date—depends on the fact that when solutions of sodium chloride and ammonium bicarbonate are mixed, double decomposition occurs, resulting in the formation of ammonium chloride and sodium bicarbonate, the latter being precipitated on account of its sparing solubility in solutions of the former. In practice, the ammonium bicarbonate is formed *in situ* by passing carbon dioxide into a brine saturated with ammonia, the reaction proceeding thus—

$$NaCl + NH_3 + CO_2 + H_2O = NaHCO_3 + NH_4Cl.$$

The ammonia is recovered by treatment of the NH_4Cl solution with lime, according to the equation—

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

The carbon dioxide is also partly recovered in the process of converting the sodium bicarbonate into the normal salt, Na_2CO_3—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

As the fundamental reaction belongs to the reversible class, the conversion of the sodium chloride is incomplete, only about two-thirds being obtained as carbonate.

The manufacture consists of two essential operations, the one being the preparation of a pure brine saturated with ammonia, the other the carbonation of this brine with lime-kiln gases and with the CO_2 recovered as indicated above.

The purification of the brine from magnesia, iron oxide, and silica, and its saturation with ammonia, are effected in the same operation in an apparatus which is typified by Fig. 9. The vessel, A, is filled with brine, and receives a charge of lime which is to precipitate the impurities above mentioned. The brine is then allowed to flow into B, where ammonia, from the still to be subsequently described, is introduced through the distributor, C, the liquor being kept cool by the water coil, D. To ensure saturation of the brine, which may have been diluted by the water accompanying the ammonia blown in, salt may be introduced through the pipe, E.

By circulation of the liquor between A and B, thorough mixture is obtained, and when saturation, as indicated by the alkalinity of test samples, is complete, the sludge is removed, mainly by decantation, in a separate vessel provided with an overflow pipe and a sludge cock. The clarification is then completed by passage through a filtering cloth before the brine

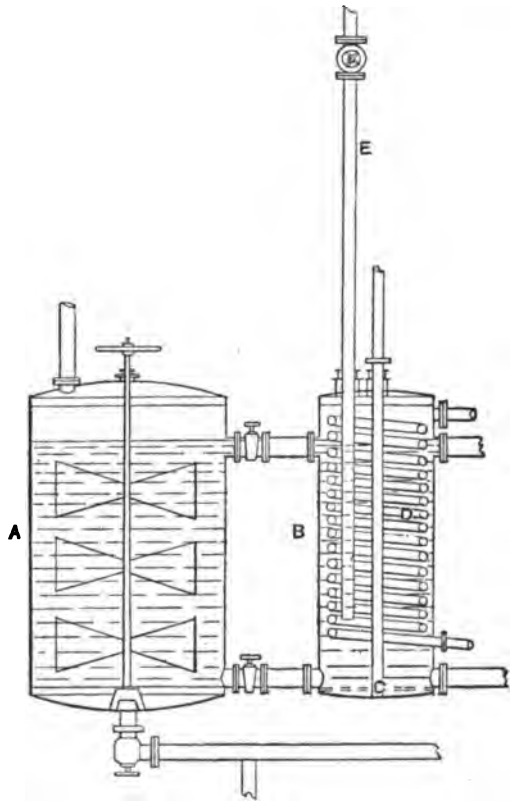


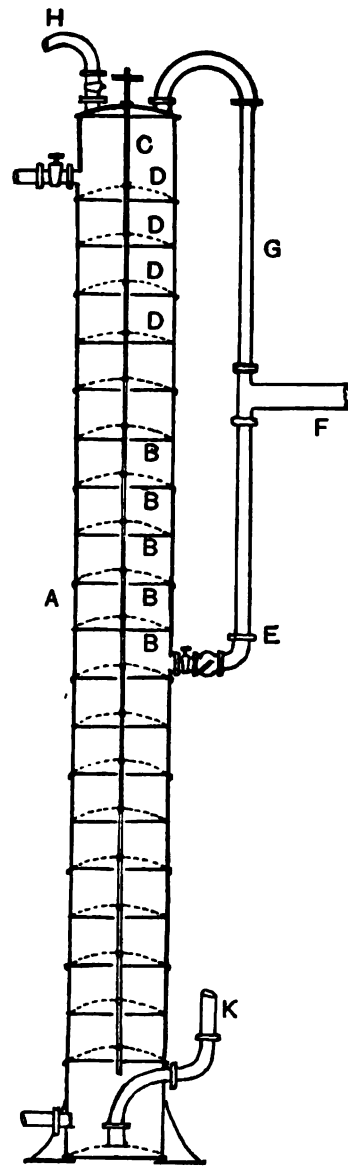
Fig. 9.—Brine saturator for ammonia-soda process.

A, Vessel for purifying brine; B, saturator; C, false-bottom distributor; D, water coil; E, salt injector.

is passed through the cooler, which consists of a series of pipes constructed on the principle of a Liebig's condenser. These movements of the ammoniacal brine are actuated by a force pump, which serves at the same time to raise it to the top of the carbonating tower.

This apparatus, represented in Fig. 10, is a cast-iron cylinder,

A, some 40 to 50 feet high, containing a number of fixed diaphragms, B, about 3 feet apart, each with a central hole through which a rod, C, passes down the whole length of the tower. To this rod are attached perforated, saucer-like plates, D, D, at such distances that they rest upon the fixed diaphragms, B. The ammoniacal brine is introduced at the middle of the tower by the pipe, E, from the storage tank, situated at the level of the main, F, about 12 feet from the top of the tower. The pipe, G, serves to equalise pressure between the main, F, and the top of the tower. It will be seen that the column is kept filled up to the level of F with ammoniacal brine, and it will be understood that by this arrangement of introducing the ammoniacal liquor at the middle of the column of liquid, the ammonia carried upwards by the ascending current will be fixed by the CO_2 which the top part of the column has already absorbed; the advantage of having ammonium bicarbonate at this part of the column arises from its being less volatile than ammonia itself, so that a smaller quantity of this valuable reagent is carried away with the waste gases through the pipe, H, than would be the case if the liquor were let into the top of the column. The introduction of



A, Cylinder; B, diaphragms; C, rod; D, D, perforated plates; E, liquor injection pipe; F, main; G, pipe for equalising pressure; H, exit pipe; K, gas injection pipe.

Fig. 10.—Carbonating tower for ammonia-soda process.

the lime kiln gases, containing about 30 per cent. by volume of CO_2, is effected by pressure through the pipe, K, at the base of the tower. A certain amount of systematic working is attained by forcing gases rich in CO_2 (*e.g.*, from the ignition of the $NaHCO_3$) into the cylinder, through this lower pipe, where they act upon nearly spent ammoniacal brine, and passing gases poorer in CO_2 through a pipe in the upper part, where they meet a richer brine. The lime kiln gases used must be cool and free from flue dust and SO_2; these objects are attained by washing with water both before and after compression. The CO_2 is generally so far used that the exit gases contain about 10 per cent., besides some ammonia which is absorbed by passage through a new batch of brine, followed by a scrubbing with sulphuric acid.

The most favourable temperature for the realisation of the double decomposition between the sodium chloride and ammonium bicarbonate is 15° C. = 59° F., and in order to maintain this as nearly as practicable, the heat of the reaction is removed by external cooling of the carbonating towers by a stream of water. It is claimed that the expansion of the compressed lime kiln gases, as they pass through the column of liquid, contributes to this cooling effect.

As the crystals of sodium bicarbonate form, they collect on the perforated diaphragms down which they slide, passing through nicks in the circumference of these, and through the central holes of the fixed diaphragms, forming a sludge at the bottom of the cylinder; a certain amount of agitation can be imparted to the diaphragms to promote the subsidence of the crystals. The sludge of crystals flows from the bottom of the cylinder on to a vacuum filter, is washed with a small quantity of water, and is then ready for conversion into soda ash.

The mother liquor and washings from the vacuum filter contain, on account of the imperfection of the reaction and the solubility of sodium bicarbonate, sodium chloride (frequently amounting to one-third of that present in the original brine), sodium bicarbonate, ammonium bicarbonate, and ammonium chloride. The mother liquor is run into the ammonia recovery apparatus (*v.i.*), and yields as final products ammonia and ammonium carbonate —which are returned to the brine saturators—and sodium chloride, which is run away. Thus, that portion of the sodium bicarbonate which remains dissolved in the mother liquor is reconverted into sodium chloride, and is run to waste.

On account of the comparatively small demand for sodium bicarbonate, the bulk of the first product of the ammonia-soda process is converted into soda ash, but a portion of it is recrystallised, to eliminate adhering ammonia, in an atmosphere of CO_2 under pressure, and sold for making baking powder, &c. The conversion into soda ash is carried out by heating the

bicarbonate in a horizontal cylinder provided with an agitator, or in retorts. The carbon dioxide, carrying the small quantity of ammonia, is returned to the lower portion of the carbonating tower. The apparent density of ammonia soda-ash is about 0·8, while that of Leblanc soda-ash is 1·2. When a dense form of soda-ash is required, a second furnacing is adopted. By reason of its mode of preparation, ammonia soda-ash is free from caustic soda, and may contain a little bicarbonate.

Caustic soda can be produced in the ammonia-soda works by causticising the ash with lime in the ordinary way (see Vol. II., p. 30), but the process is more costly than with Leblanc soda, because in the latter case, as has been shown, the crude soda-ash contains a considerable amount of caustic soda; this finds its way into mother liquors which have no analogue in the ammonia-soda process, where what mother liquor there is (from the carbonating towers) must be used for the recovery of ammonia, in the course of which operation the sodium bicarbonate contained in the liquor is decomposed. A method of causticising dry soda-ash is, therefore, of special value for the ammonia-soda process. The most promising consists in heating soda ash with ferric oxide, whereby CO_2 is expelled and a loose compound of Na_2O and Fe_2O_3, sodium ferrite, is formed. This is decomposed on treatment with water, giving a concentrated soda-lye and ferric oxide which can be used over again. The evaporation of the concentrated soda-lye is a comparatively economical process.

Production and Recovery of Ammonia.—The process for the recovery of ammonia in the ammonia-soda process does not essentially differ from that adopted for the preparation or recovery of ammonia in other industries—*e.g.*, the preparation of ammonium sulphate at the gas works. The following general description of the apparatus employed will, therefore, apply to all cases where this gas is produced or recovered :—

Most sources of crude ammonia contain ammonia as such, ammonium carbonate, frequently sulphide, and non-volatile ammoniacal salts. The first three of these constituents are sufficiently volatile to be expelled when the liquor is heated, therefore the fraction of ammonia thus obtained is known as "free ammonia," while the non-volatile salts must be heated with some base stronger than ammonia—*e.g.*, lime—the fraction liberated in this manner being known as "fixed ammonia."

A still adapted for general use consists of two portions, the one arranged for the expulsion of "free ammonia," the other for the liberation of "fixed ammonia." The separation of a more from a less volatile substance, such as ammonia from water, is best effected by the process of fractional distillation, which is always aided by some kind of dephlegmator; in ammonia stills, as in alcohol stills, this takes the form of a fractionating column.

The liquor containing free and fixed ammonia is run through the pipe, A (Fig. 11), into the fractionating column, B, the internal construction of which is similar to that used for distilling spirit, and is described in the section dealing with this subject. During its passage down this tower, the liquor en-

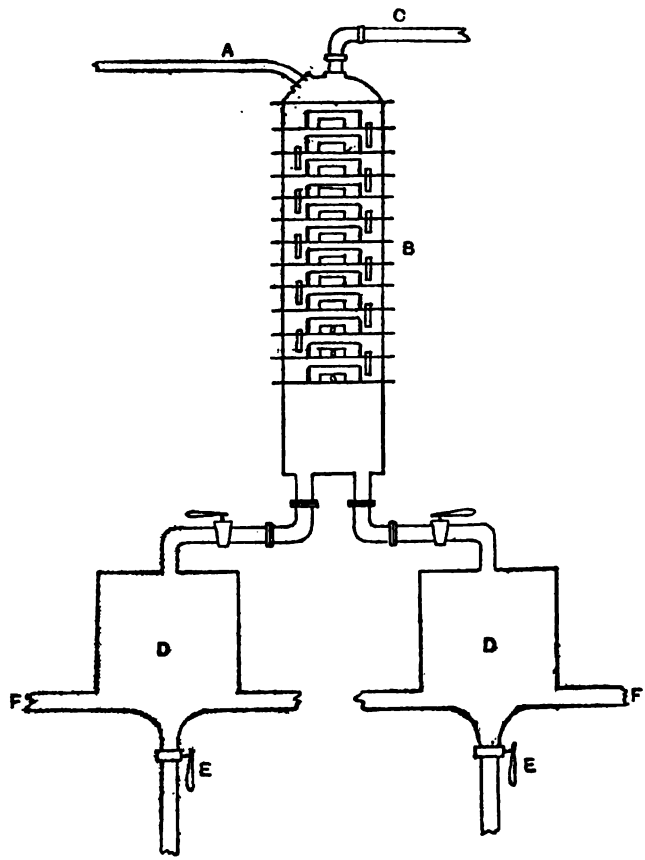


Fig. 11.—Ammonia still.

A, Liquor inlet; B, dephlegmator; C, gas exit pipe; D, D, stills; E, E, sludge cocks; F, lime inlet.

counters a current of steam, and, becoming heated, parts with its volatile ammonia together with other gases, the products of the dissociation of volatile ammonium salts, such as H_2S and CO_2. These gases pass away by the pipe, C, and if the ammonia is to be converted directly into ammonium sulphate, as is the

case at a gas works, it is sent into the saturator containing sulphuric acid, as described in the section on gas manufacture. When the ammonia is used to saturate brine in the ammonia-soda process (*v.s.*) it needs no further treatment, inasmuch as only ammonia and carbon dioxide are present.

From the bottom of the fractionating column, the liquor, containing the fixed ammonia, enters the still proper, D, D. For continuous working several such stills are used, so that one may be in operation while another is being emptied, a system of distributing-pipes and cocks serving to connect each at will with the column. The lime necessary for freeing the ammonia is introduced into the stills, either as milk of lime through a pipe, F, or as lumps contained in an iron cage. The whole apparatus is heated by the injection of steam, the heat necessary to liberate the fixed ammonia and to work the rectifying column, being thus obtained. The spent sludge is run off from D by a sludge cock, E, at the bottom of the still; in the case of the ammonia-soda process the "sludge" consists chiefly of calcium chloride, together with some sodium chloride derived from the decomposition of the sodium bicarbonate remaining in solution after the bulk of this salt has separated in the carbonating towers. This decomposition occurs thus—

$$NaHCO_3 + NH_4Cl = NaCl + NH_3 + H_2O + CO_2.$$

Such sodium chloride as has escaped conversion in the carbonating towers (*v.s.*) will also be in this sludge liquor.

Recovery of Chlorine in the Ammonia-Soda Process.—Whereas in the Leblanc method of making soda, one-third of the chlorine in the original salt is recovered as an essential part of the working cycle, in the ammonia-soda process none is obtained by the ordinary manner of working. Various suggestions have been made to remove this drawback. According to the method of working described above, the chlorine appears finally as calcium chloride, this plan being obligatory from the necessity of recovering ammonia. An obvious economy consists in the direct recovery of both the constituents of ammonium chloride—viz., NH_3 and HCl—which is rendered the more feasible on account of the ease with which ammonium chloride is dissociated on volatilisation. No practicable method of separating the NH_3 and HCl in the dissociated ammonium chloride having yet been devised, it is, therefore, necessary to employ some base capable of combining with the HCl. The base chosen for this purpose must be sufficiently feeble to allow of decomposition of the corresponding chloride on heating in air. Most of the basic oxides, save the alkalies and alkaline earths, fulfil this condition, but magnesia presents many advantages over others that could be used.

One of the best methods of this class is that devised by

Mond. The liquors from the ammonia-soda process are cooled considerably below 0° C. = 32° F., and the ammonium chloride which separates, together with some salt and sodium bicarbonate which do not interfere, is volatilised in antimony-lined vessels (which resist its attack), and passed over heated (400° C. = 752° F.) magnesia, whereby magnesium chloride and ammonia are formed. The latter is returned to the ammonia-soda plant, and the former is heated at 800° to 1,000° C. = 1,472° to 1,832° F. in air supplied from a Cowper's hot-blast stove (see *Iron*, Vol. I., p. 131), whereby it is decomposed into magnesia and chlorine. It is claimed that gases containing 7 to 10 per cent. of chlorine are thus obtained. The magnesia serves for repetition of the process.

The ease with which magnesium chloride (and in a smaller degree calcium chloride) is decomposed by being heated in air, may be utilised for the recovery of chlorine from the still liquor of the ammonia recovery process. In the case of calcium chloride, the comparative stability of this substance militates against success.* By substituting magnesia for lime in the ammonia stills, magnesium chloride appears in place of calcium chloride and can be treated by the Weldon-Péchiney method.

This process, which may also be applied both to obtaining chlorine from aqueous hydrochloric acid by previously converting it into magnesium chloride, and for the manufacture of chlorine from the waste magnesium chloride obtained in working up Stassfurt salts (see *Potash*, Vol. II., Chap. XVIII.), consists essentially of three stages. In the first, magnesium oxychloride is synthesised by grinding magnesia with a strong solution of magnesium chloride, the composition of the moist mass approximating to the formula $5MgO.4MgCl_2$. This oxychloride is reduced to pieces of the size of a walnut, and dried by passage on waggons through a heated chamber at 300° C. = 572° F. The dried oxychloride, which has lost half its water and some 5 to 8 per cent. of its chlorine as HCl during the drying, is filled into narrow firebrick chambers previously heated by a locomotive regenerative furnace to a temperature of about 1,000° C. = 1,832° F., and heated air is passed over it. 45 per cent. of the chlorine is thus evolved free, 40 per cent. as HCl (derived by the action of the residual water in the dried oxychloride), and the balance remains in the residue, which is cooled and returned to the process. The escaping gases, containing some 6 to 8 per cent. of chlorine, the remainder being HCl, N, and surplus air, pass into a condenser consisting of a stone tower filled with a number of cross tubes of glass, through which water is circulated. Here the water is

* The decomposition of calcium chloride is aided by the presence of an acid oxide, the cheapest that can be applied being silica, thus :—

$$CaCl_2 + SiO_2 + H_2O = CaO.SiO_2 + 2HCl.$$

condensed, and the gases next pass through a series of bombonnes, and finally through a coke scrubber, in order to condense fully the HCl. The chlorine is utilised for making bleach and chlorates.

III. OTHER CHEMICAL PROCESSES FOR MAKING ALKALI.

Several other processes for making alkali have been devised, but their application has been limited. They depend upon the following general principles:—(1) The decomposition of a sodium salt by means of a base capable of forming an insoluble precipitate with the acid of the sodium salt, such as is expressed by the equation—

$$Na_2SO_4 + Ba(OH)_2 = 2NaOH + BaSO_4.$$

(2) The treatment of a sodium salt at a high temperature with an acid radicle capable of displacing the radicle in the sodium salt at that temperature, and of forming a new sodium salt, decomposable by water or CO_2, thus—

$$(1)\ 2NaCl + SiO_2 + H_2O = Na_2SiO_3 + 2HCl.$$
$$(2)\ Na_2SiO_3 + CO_2 = Na_2CO_3 + SiO_2.$$

A process of this class, which has been put into actual work, is the **Cryolite Process**, in which sodium carbonate is produced as a bye-product in the manufacture of aluminium sulphate—

$$3NaF.AlF_3 + 3CaCO_3 = Na_3AlO_3 + 3CaF_2 + 3CO_2.$$

In this case the alumina functions as an acid oxide, yielding sodium aluminate, which can be decomposed in aqueous solution by CO_2—

$$2Na_3AlO_3 + 3CO_2 = 3Na_2CO_3 + Al_2O_3,$$

the alumina being subsequently converted into aluminium sulphate.

The principles of methods (1) and (2) may be combined, as in the Staveley process, in which sodium sulphate is treated with calcium carbolate, $(C_6H_5O)_2Ca$, made by agitating crude carbolic acid with milk of lime; the reaction proceeds thus—

$$Na_2SO_4 + (C_6H_5O)_2Ca = 2C_6H_5ONa + CaSO_4.$$

The sodium carbolate thus obtained is decomposed by CO_2, crude carbolic acid being regenerated—

$$2C_6H_5ONa + CO_2 + H_2O = Na_2CO_3 + 2C_6H_5OH.$$

Alkali, Bleach, and Chlorates produced by Electrolysis.—When fused sodium chloride is submitted to electrolysis, chlorine is evolved at the anode and metallic sodium at the cathode; in the presence of water the sodium is never liberated

as such, because of the immediate formation, in its place, of caustic soda and hydrogen, HOH + Na = NaOH + H. In an open cell the hydrogen thus evolved tends to combine with the chlorine by diffusion through the liquid, and HCl (and finally NaCl) is regenerated; a similar contact of the anode and cathode products—namely, chlorine and caustic soda—gives rise to the formation of sodium hypochlorite and sodium chlorate (see *Electrolytic bleaching*, Vol. II., Chap. XII.). It follows that when caustic soda and chlorine are to be produced, the anode and the cathode products must be separated—*e.g.*, by a porous septum. The decomposition of sodium chloride under these conditions may be represented by the equation—

$$NaCl + HOH = \underbrace{NaOH + H}_{\text{Cathode.}} + \underbrace{Cl.}_{\text{Anode.}}$$

The voltage of the current, and, therefore, the total electrical energy needed to decompose a solution of salt, is necessarily greater when hydrogen is liberated, and chemical work thus done, than when the evolution of hydrogen is prevented; in some systems the hydrogen is oxidised by the use of an oxidant, such as copper oxide, which can be readily regenerated by heating in air; in this case the superfluous work done is represented finally by the reduction of CuO to Cu, instead of by the more energetic reduction of H_2O to H_2. In practice, too, it is advantageous to suppress this hydrogen, for mechanical reasons.

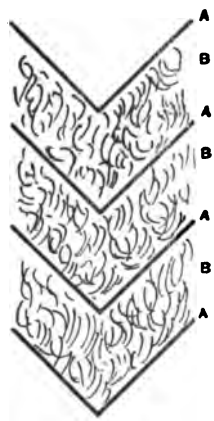


Fig. 12.—Diaphragm for electrolytic process of making alkali.

A, V-shaped slats; B, asbestos.

The simplicity of the production of alkali and chlorine by electrolytic methods is largely discounted by the difficulty of finding a material capable of withstanding the action of nascent chlorine, and of constructing a diaphragm efficient to prevent mixture of the liquids on each side, and yet of low electrical resistance.

These difficulties are met, in the Greenwood process, by the use of an anode of plates of retort-scurf (gas carbon) coppered on one side and cast to a core of type-metal, in order that a large plate of this refractory form of carbon may be made. The diaphragm consists of a series of V-shaped slats (A, Fig. 12) packed with asbestos (B). An iron plate can be used as the cathode where there is no corrosive action. The process is continuous, separate supplies of brine being circulated through the anode and the cathode compartments, chlorine being given off in the

former, while the liquor in the latter becomes enriched with caustic soda, until a concentration is attained at which the liquid can be economically evaporated, the salt being fished out and the caustic soda finished in the usual way. The chlorine, which is of full strength, can be used for making bleach by the methods already described. No attempt is made to utilise the hydrogen.

Other systems are similar in arrangement, but differ in mechanical details (see *Sodium*, Vol. I., p. 226).

The direct production of chlorates by electrolysis becomes possible if the electrolyte be hot and the chlorine and alkali allowed to commingle. The method of suppressing hydrogen with copper oxide is here convenient, as the use of a diaphragm may be then dispensed with and intermixture facilitated. The reaction takes place on the following lines:—

$$6KCl + 3H_2O = KClO_3 + 5KCl + H_6.$$

The advantage of this method is that a cheap potassium salt (the chloride) can be directly converted into chlorate.

REVIEW OF THE PROCESS OF ALKALI MANUFACTURE.—The keen competition between makers of alkali by the Leblanc and the ammonia-soda process lends special interest to the consideration of the chemical reasons for their relative success. In both cases NaCl, the only practicable source of soda, has to be converted into Na_2CO_3, a process involving the absorption of energy, some idea of the amount of which may be gathered from our knowledge that the quantity of energy in terms of heat which would be required to produce Na_2CO_3 from NaCl by the simplest conceivable process, expressed by the equation—

$$2NaCl + O + CO_2 = Na_2CO_3 + Cl_2$$

is 19·6 Cals. The only known method of doing this amount of chemical work directly, is by the use of electrical energy. Electrolysis has not hitherto been remuneratively applied for the manufacture of alkali and chlorine, not only because of the practical difficulties mentioned on p. 52, but on account of the fact that the energy requisite has to be obtained circuitously by the combustion of coal beneath a boiler, and by engine and dynamo as intermediaries (see Vol. I., p. 93); this process of conversion of heat into electricity is of low efficiency. Another difficulty, at present encountered, is the large and costly plant required for a comparatively small output. Failing electrolysis, the requisite energy must be supplied by stages. The energy changes of these stages may be briefly considered.

In the Leblanc process, the formation of salt-cake is an exothermic reaction, the energy for which is derived from the sulphuric acid (itself containing the energy evolved by the combustion of sulphur, which has been imparted to it during the

concentration in the Glover tower). In the black ash furnace the energy absorbed in the reduction of Na_2SO_4 to Na_2S is furnished by the fuel. There is but little energy involved in the double decomposition between $CaCO_3$ and Na_2S. Thus, in the Leblanc process the chemical energy of the sulphur has been utilised in the process, and restored in the black ash furnace, for the sulphur can be recovered from calcium sulphide without the expenditure of any considerable quantity of fresh energy.

In the ammonia-soda process the main reaction, involving the conversion of sodium chloride into sodium bicarbonate, does not require the application of external energy, but the conversion of sodium bicarbonate into sodium carbonate—that is, the same end-product as in the Leblanc process—requires the application of energy in the form of heat. The only other cause of the expenditure of energy occurs in the liberation of ammonia from ammonium chloride, which is brought about by the action of lime prepared by the dissociation of $CaCO_3$ into CaO and CO_2, the energy having its origin in the consumption of fuel. The fact that the CO_2 produced during the burning of the limestone is necessary in the process, contributes to economy of energy, as well as of material.

It will be clear from this, that the expenditure of energy, in the form of fuel, is considerably less than that needed for the Leblanc process. The balance against the Leblanc process is, however, not all waste, as a portion appears in the form of the chemical energy of HCl, whereas calcium chloride is the corresponding product in the ammonia-soda process; the difference in the chemical energy of these two compounds is well illustrated by the relative ease with which chlorine can be obtained from them. It is this difference which enables the Leblanc process to retain its footing, in spite of the cheaper production of *alkali* by the ammonia-soda process. The improvement of such methods as the Weldon-Péchiney for the treatment of the residual chloride of the ammonia-soda process, tends to nullify this advantage. Before the successful recovery of sulphur (Chance process) was practised, the Leblanc process was at a still greater disadvantage, for at that time energy was expended nearly sufficient to recover the sulphur, which was nevertheless thrown to waste as calcium sulphide. Attention has already been called to the greater ease with which caustic soda is produced from Leblanc soda-ash than from ammonia soda. The reason why caustic soda and bleach are best prepared by the Leblanc method, and pure soda-ash by the ammonia-soda process, will be evident from contemplation of the above considerations.

CHAPTER III.

DESTRUCTIVE DISTILLATION.

General Principles.—The term destructive distillation is applied to the process of heating a complex substance to its point of decomposition. This is generally accomplished by performing the operation in a closed retort, as in coal-gas manufacture, but may be effected by the limited combustion of the substance to be distilled, so that the heat generated destructively distils the remainder, as in charcoal burning and the manufacture of blast-furnace coke. The class of substances usually treated are such carbon compounds as are split up at a high temperature with the evolution of gaseous and liquid products, a residue relatively richer in carbon being left—a change which is indicated by the term "carbonisation." Such bodies are coal, shale, and wood.

It will be understood that the essential difference between the process of destructive distillation and that of ordinary distillation (such as that of alcohol), consists in the fact that the substances collected in the receiver in the former operation do not pre-exist in the retort—they are *products* of the process, not *educts*.

The nature of the products obtained is dependent on temperature, and, in a minor degree, on pressure. E. J. Mills has drawn attention to the fact that at high temperatures aromatic hydrocarbons—*e.g.*, those of the benzene and homologous series—predominate in the liquid products, while at low temperatures hydrocarbons of the fatty or paraffin series are present in greater amount. To the kind of change caused by destructive distillation, the same author applies the term "cumulative resolution," by which he means the polymerisation of the substance distilled in conjunction with the removal of water from it; thus cellulose, $n(C_6H_{10}O_5)$, (the typical constituent of wood), may be viewed as suffering decomposition by the following steps:—

$$C_6H_{10}O_5 - H_2O = C_6H_8O_4.$$
$$C_6H_8O_4 - H_2O = C_6H_6O_3.$$
$$C_6H_6O_3 - H_2O = C_6H_4O_2.$$
$$C_6H_4O_2 - H_2O = C_6H_2O.$$
$$C_6H_2O - H_2O = C_6.$$

He considers that the organic matter in coal and shale contains

carbon which may be represented as existing in groups of C_3, so that its ultimate composition, as far as the carbon is concerned, is expressed by nC_3. This group, he states, can be traced in the products of destructive distillation. It has to be noted, however, that it has been shown by Ramsay that pure cellulose yields acetic acid and methyl alcohol among its products of destructive distillation, and that their formation can scarcely be explained by the example of cumulative resolution given above. The whole question in its theoretical bearings is complicated by the fact that the substances which it is customary to distil destructively are mixtures, and that numerous interdependent reactions no doubt take place. Thus, in the destructive distillation of wood, an exothermic change occurs at one point of the reaction, while with pure cellulose no such effect has been observed. A change of this kind may be attributed to the oxidation of a portion of the hydrogen or carbon of the material distilled, at the expense of another portion richer in oxygen, the reaction being induced by the attainment of a particular temperament. Whatever be the precise mechanism of the changes involved in destructive distillation, the products usually include hydrogen, water, carbon monoxide and carbon dioxide; gaseous, liquid and solid hydrocarbons of several series and their oxygen derivatives; ammonia, organic bases, and cyanides (if the substance contain nitrogen); and sulphuretted hydrogen, carbon bisulphide, sulphocyanides, and bodies of which thiophen is a type (should sulphur be present). It is to be noted that the oxygen derivatives generally precede hydrocarbons in the order of distillation. The characteristic products for those classes of substances which are destructively distilled on an industrial scale, and the conditions governing their formation, will be dealt with under separate headings. It suffices to state here that when wood, brown coal, and bituminous shale are distilled, the products are chiefly of the paraffin series, and that when coal is distilled they are mainly aromatic.

I. DESTRUCTIVE DISTILLATION OF COAL.

Kinds of Coal.—The various kinds of coal have been already classified in Vol. I., p. 49, and repetition is unnecessary. The class of coal used for destructive distillation is known, according to Grüner's classification, as "caking coal burning with a long flame." The average composition ranges from carbon 80 to 85 per cent., hydrogen 5 to 5·8 per cent., oxygen and nitrogen 10 to 14·2 per cent. These numbers are calculated on the coal free from ash, which averages 5 per cent. Coals of this character are hard, tough, dark, and lustrous, and have a specific gravity of 1·28 to 1·30. Various English gas coals exhibit considerable

deviations from these values, and could hardly be classed under Grüner's system. The following may be quoted:—

	Sp. Gr.	C.	H.	S.	N.	O.	Ash.	H_2O.
Newcastle gas coal, .	1·26-1·33	80·2-84·3	4·6-5·3	0·8-1·3	0·9-1·7	4·3-9·2	1·4-5·6	1·1-1·7
South York silkstone,	1·26	80·3-82·0	5·0-5·7	1·2-1·6	1·7-1·9	5·2-7·2	2·3-3·3	0·9-1·3
Derbyshire silkstone,	...	75·7-76·9	5·0-5·8	2·3-2·4	1·6-1·7	5·6-7·5	3·0-4·4	3·6-3·9
Barnsley gas coal, .	...	75·6-76·6	4·8-5·0	1·3-2·8	1·6-1·7	6·9-7·5	3·9-4·6	0·8-3·5
Cannel, .	...	69·0	8·8	1·3	1·9	8·9	10·1	...

The mere analysis of a coal does not suffice to determine its value for gas making, and it is, therefore, customary in gas works to put a small quantity through the whole process of distillation, in an apparatus similar to that used on the large scale, when both the quantity and quality of the gas and coke are determined. The yield and quality of both are dealt with in two subsequent sections. Cannel yields a gas of higher illuminating power than does gas coal, and it is used for enriching coal gas obtained from the latter.

It should be added, however, that Deville has shown that there is a certain connection between the composition of gas coals and the nature and quality of the products of their destructive distillation. The following table exhibits the composition of typical gas-making coals, calculated for the pure coal substance, free from ash and water:—

	I.	II.	III.	IV.	V.
Carbon, . . .	88·38	86·97	85·89	83·37	81·66
Hydrogen, ...	5·06	5·37	5·40	5·53	5·64
Oxygen, . . .	5·56	6·66	7·71	10·10	11·70
Nitrogen,* . . .	1·00	1·00	1·00	1·00	1·00

Of these coals, that represented in column III. has the composition typical of the best gas coal; it yields a large quantity of gas and coke of good quality. Coals I. and II. give much coke, but poor gas. Coals IV. and V. give gas of high illuminating power, but a small quantity of coke, and that of poor quality. The yield of coke decreases with the increase of oxygen in the coal, whereas the quantity of tar and liquor increases.

* Assumed value.

The amount of aromatic hydrocarbons in the products appears to be independent of the content of the coal in oxygen, sulphur, and ash.

(A.) **CARBONISING IN RETORTS FOR GAS PRODUCTION.**—The system essentially consists in heating the coal in a fireclay retort of elliptical or of ⌀ section, set in a furnace heated by producer gas. Formerly a furnace burning solid fuel—part of the gas coke—was used, but greater economy is obtained by using the coke in a producer, 10 to 15 per cent.

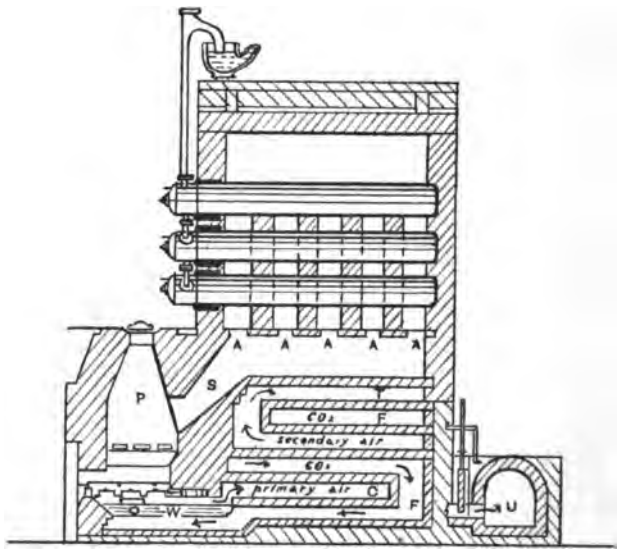


Fig. 13.—Gas retort furnace.

P, Producer; W, water pan; C, primary air channel; T, secondary air channel; F, F, exit flues; U, chimney; A, A, A, A, combustion channels.

of coke, reckoned on the weight of coal carbonised, sufficing, instead of 25 to 40 per cent. The temperature of carbonisation is also higher; this, however, contributes to the production of a less valuable tar, which being, moreover, more viscid, causes obstructions more readily. For the use of coke in a producer, see Vol. I., p. 65. A section of a typical retort of modern design is shown above. Its average dimensions are 9 to 10 feet long, 16 to 22 inches wide, 13 to 16 inches in height, and the walls have a thickness of 3 inches in the middle and 4 inches at the mouth. It is closed by a cast-iron mouthpiece projecting about 16 inches from the furnace (Fig. 13), bolted on to the thick fire-

clay end, and provided with an "ascension pipe," 6 to 7 inches in diameter, and with a cast-iron door fitting on a bedplate, made air-tight by a lever hinge. Nowadays, retorts of double this length, with two mouths ("through retorts"), each with its appropriate fittings, are used, and are charged from each end. The mode of setting is shown in the illustration. In the case of the through retorts, separate furnaces and flues are used for each half.

The method of heating is as follows:—An ordinary producer, P (Fig. 13), fed with the coke as it is drawn from the retorts (*v.i.*), is built close to the bench of retorts, the distance being the least possible to prevent loss of heat from the producer gas in passing

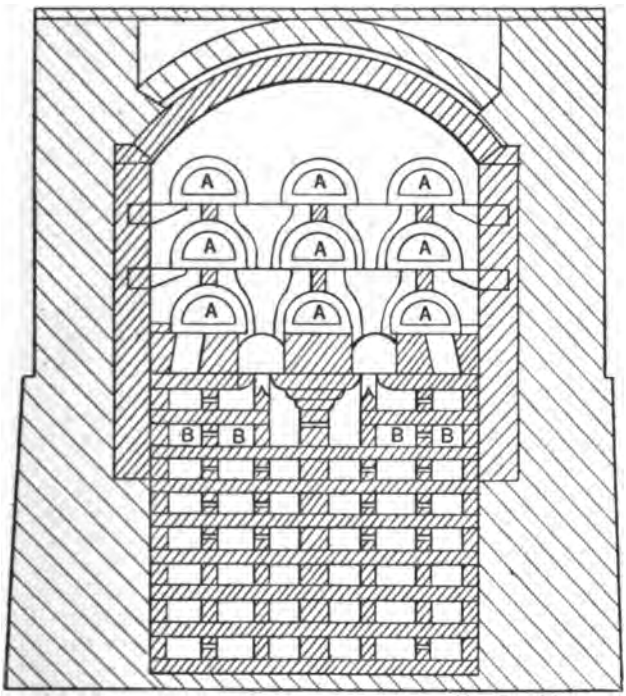


Fig. 14.—Setting for gas retorts.

A, A, Section through retorts; B, B, section through regenerator channels.

to the space surrounding the retorts. A primary supply of air is drawn over a pan of water, W, placed beneath the fire-bars of the producer, but separated from these by a plate. It then passes through a firebrick channel, C, heated by contact with the flues conveying the products of combustion from the chamber containing the retorts, and is thereby heated to about 500° C.

= 932° F.; from this channel it enters the producer, where it forms gas of the average composition—CO 20·6, H 15·0, CO_2 8·6, N 55·8. This gas at the temperature of 1,150° C. = 2,102° F. passes up the channel, S, where it mixes with the "secondary" air (which is at a temperature of 1,000° C. = 1,832° F.), drawn in through the channel, T, heated by the exit gases passing through the neighbouring flues, F, F. In contact with this second supply of air the CO and H burn to CO_2 and H_2O, and the flame plays round the retorts through the channels, A, A, A, A, the exit gases going to the chimney, U, by way of the flues, F, F, the walls of which are used for heating the secondary air supply, at a temperature of 1,400° C. = 2,552° F.

A cross section through both retorts and regenerator is shown in Fig. 14, the former being represented at A, whilst the latter is shown at B.

Charging and Drawing.—This is still generally effected by hand, the coal in quantities of 2 to 3 cwts. being introduced into the retort by means of a long scoop, the operation taking about forty seconds. At the end of the distillation the coke is drawn by long iron rakes, and, where the gaseous system of heating is in use, a portion falls directly into the producer, and the rest is quenched, while the retort is immediately recharged. Mechanical charging and drawing are, however, largely used.

West's system involves the use of an automatic scoop; to this the objection that it damages the retorts has been made. Other systems require the use of inclined retorts set at such an angle (about 30°) that the charge will fall out (after exhaustion) when dislodged by a slight push. The charging is effected from the top through a hopper, the angle of incline favouring the even distribution of the charge.

The Process of Distillation.—The quantity and quality of volatile products obtained, and the time occupied by the distillation, are largely dependent upon temperature. This generally ranges from 616° C. to 980° C. = 1,141° to 1,796° F., and even to 2,000° F. = 1,093° C., in a six-hour charge. The quantity of gas varies from 10,000 to 12,000 cubic feet per ton. The influence of temperature upon the quantities of gas and tar produced is generally seen in the larger volume of gas evolved at high temperatures, and the smaller amount of tar. The following table exhibits the yield of coke obtained from the coals mentioned on p. 57; it varies but slightly with the temperature:—

	Percentage Coke.
Newcastle gas coal,	67
South Yorkshire silkstone,	66
Derbyshire silkstone,	64
Barnsley gas coal,	64
Cannel,	50

Besides the carbon left as coke, there is a portion, constituting,

however, but an insignificant fraction of the whole, left as a dense coherent coating (retort scurf, retort carbon, or gas carbon) on the interior of the retorts. This is produced by the decomposition of a part of the gaseous hydrocarbons evolved from the coal, and is useful as rendering the retort impervious to the gas, even though it crack, and harmful as reducing the capacity of the retort and hindering the access of heat to the coal from without. Chemically, a disadvantage accrues from this decomposition ("cracking," see *Petroleum*, Vol. II., Chap. V.) of illuminating hydrocarbons to a point at which they deposit carbon—a decomposition which should be delayed until the hydrocarbons are burnt in an illuminating flame; *per contra*, heavy hydrocarbons that would otherwise condense in the tar are cracked with the formation of less condensible gaseous illuminants. As an example of this disadvantageous cracking, the following figures, which show the percentage of hydrocarbons and of hydrogen in the gas at different periods of the distillation, may be quoted:—

Lapse of Time after Charging.	Hydrocarbons.	Hydrogen.
	Per cent.	Per cent.
10 minutes.	68	20
1½ hours.	50	38
3½ ,,	36	52
5½ ,,	24	67

Experiments on a large scale have been made on the effect of the addition of slaked lime to the coal before its introduction into the retort; the amount added is 2·5 per cent.; it is claimed that the yield of gas is thereby increased to the extent of 5 per cent., but it is of 5 per cent. smaller illuminating power; the proportion of ammonia obtained with the tar is also increased in many cases from 20 to 50 per cent. of the amount ordinarily obtained, but this depends largely on the nature of the coal, no increase being sometimes observed. One of the principal objects of liming the coal is to increase the yield of ammonia; that there is a large margin for improvement in this respect is shown by the following table giving the proportion of nitrogen usually appearing as ammonia and in other forms:—

	Per cent. of Total Nitrogen.
Evolved as ammonia, ...	14·50
,, cyanogen, ...	1·56
,, uncombined nitrogen, ...	35·26
Remaining in coke, ...	48·68
	100·00

In spite of the multiplicity of the substances obtained during the process of destructive distillation, as already enumerated, they are commercially divisible into gas, tar (together with ammoniacal liquor), and coke. It follows from the general statements which have been made in the introductory section, that these products represent stages characterised by an increase in the content of carbon. Thus the gas contains as typical constituents, hydrogen and hydrocarbons of the paraffin series; the tar is characterised by hydrocarbons of the benzene and still further condensed series; while the coke approximates in composition to carbon free from hydrogen. Their formation is, however, not successive but simultaneous, so that arrangements are necessary for separating them as they are produced. At the same time it is necessary to remove from the gas various constituents which would be objectionable in its use for lighting and heating. Both objects are attained by plant whose arrangement is typified in Fig. 15, and which will be described before considering the products themselves in detail.

Plant.—The volatile products are drawn from the retorts, A, by the exhausters, B (see below), through the ascension pipes, C, and the water contained in the hydraulic main, D, which is common to all the retorts, and whose function is to remove the less volatile portions of the tar and any solid matter, such as already condensed naphthalene and solid carbonaceous material carried over mechanically. A further use of this main is to serve as an hydraulic seal for the dip pipes, E, as the downward portions of the ascension pipes are termed; these are immersed to the depth of 1 to 1½ inches. This seal prevents the gas finding its way back into the retort when the latter is opened for charging. The products condensed in the hydraulic main are conveyed away by a pipe called the foul main (leading from the end of the hydraulic main), and are treated together with the rest of the tar. Another pipe, F, at the upper part of the hydraulic main conveys the gas to the condenser, which may be an air condenser, G, consisting in older plants of a series of vertical cast-iron pipes connected by ∩-shaped heads at the top, and set into a horizontal box with partitions between each adjacent pair, so that the liquid products are collected and the gaseous are free to pass throughout the system. This arrangement has the objection that the air warmed by contact with the lower part of each pipe rises, and by displacing the cold air hinders condensation: in modern practice this is met by arranging the pipes horizontally (see Fig. 15). Water-cooled condensers differ from the above in that the gas passes up a tower containing a number of vertical iron pipes through which water circulates in a direction contrary to that of the gas. In most English works the air condensers are still preferred.

In English practice the exhauster (Beale's rotatory exhauster, B)

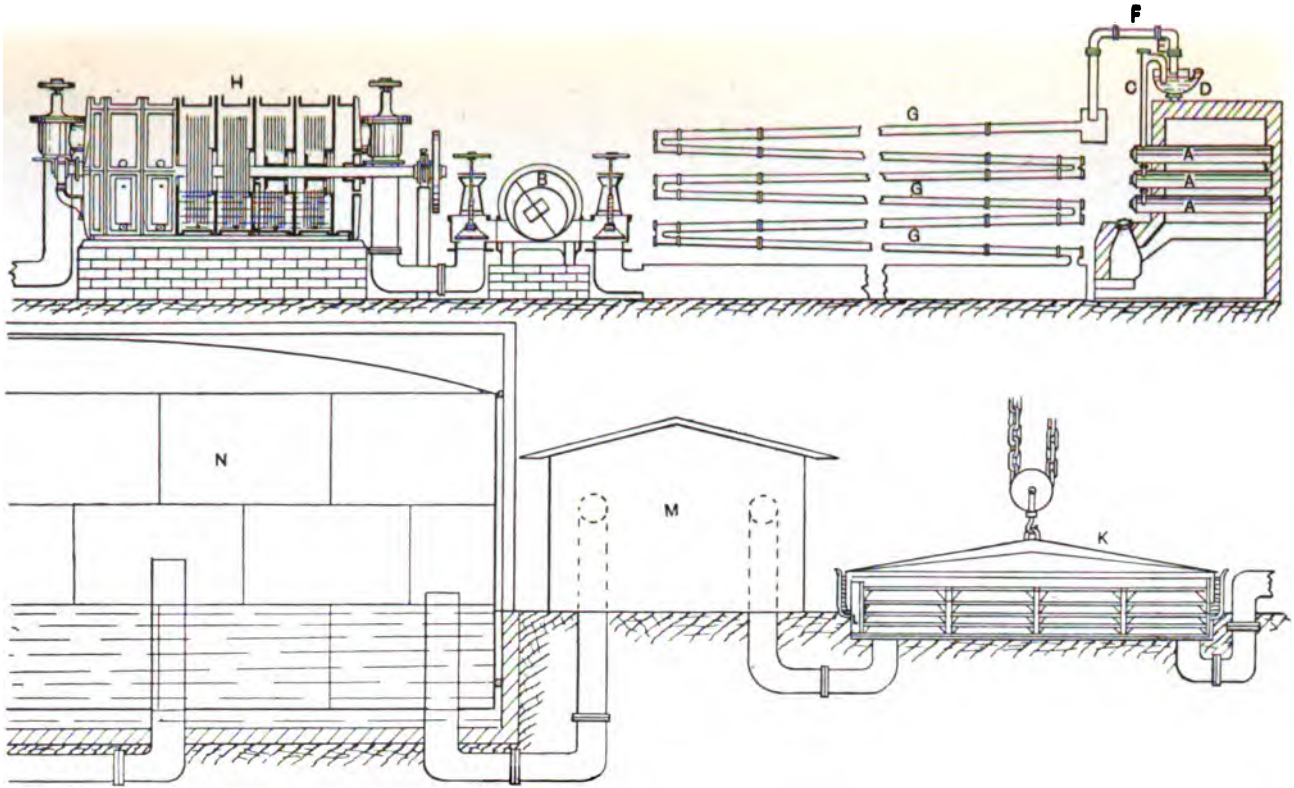


Fig. 15.—Gas manufacture plant.

A, A, Retorts; B, rotatory exhauster; C, ascension pipe; D, hydraulic main; F, dip pipe; G, G, condensers; H, washer; K, purifier; M, station meter; N, gasholder.

is a drum in which a second drum revolves, set eccentrically to the outer drum, and carrying a slide traversing the inner surface of the outer drum, thus pulling the gas from the retorts and pushing it to the succeeding portions of the plant, and is placed directly after the condensers. Other systems (*e.g.*, the Körting) which are much used on the Continent involve contact with water in the exhausters; these are, therefore, placed after the scrubber in order that the valuable ammonia may not be absorbed by the water they contain.

The scrubber, or washer, H, is designed to extract the ammonia from the gas; at the same time it removes a portion of the CO_2, H_2S, cyanogen, and sulphocyanogen. In its older form it consists of towers filled with wooden chequer-work or packed with coke, or provided with perforated horizontal plates, over which water is sprayed by a distributor at the top.* The gas ascends and is washed by the descending water. The clogging of the towers and the formation of channels among the packing thereof cause a loss of efficiency, so that other forms (such as that shown in the figure) are used, in which water is continually agitated with the gas in a cylinder by means of parallel metal discs attached to an axial shaft, which revolves at the surface of the water, so that one-half of each plate is continually exposing a freshly wetted surface to the gas. All methods of washing should be systematic—*i.e.*, the water should travel through the washers in a direction the reverse of that of the gas.

Much of the H_2S, CS_2, HCN, HSCN, and CO_2 still remains in the washed gas, and has to be removed by passage through the purifiers, K. Two purifying materials are in common use—namely, slaked lime and hydrated ferric oxide. Neither of these is perfectly efficient alone nor capable of completely removing CS_2; but this latter object can be effected by lime which has been partially saturated with H_2S, and thus converted into calcium hydrosulphides ($Ca(SH)(OH)$ and $Ca(SH)_2$).

The hydrated ferric oxide removes H_2S thus—

(1) $Fe_2O_3 . H_2O + 3H_2S = Fe_2S_3 + 4H_2O$.
(2) $Fe_2O_3 . H_2O + 3H_2S = 2FeS + S + 4H_2O$.

The first is the chief reaction. The advantage of the hydrated ferric oxide over lime, which would also remove H_2S, is that the mixture of Fe_2S_3 and FeS can be taken out of the purifier and exposed to the air whereby it is "revivified" in accordance with the following equations, in which the water is not expressed:—

(1) $Fe_2S_3 + O_3 = Fe_2O_3 + S_3$.
(2) $FeS + O = FeO + S$.

The FeO becomes converted into Fe_2O_3 upon further exposure.

* In large works the gas is generally "roughed" in some such washer as the Livesey, which consists of a tank with baffle plates to divide up the gas, and is finished in tower scrubbers. The washer-scrubbers described above are sometimes used alone.

The oxide can be used repeatedly until it is "spent"—*i.e.*, until it contains so much sulphur (50 per cent.) and other impurities as to be inoperative. The revivification can be effected simultaneously with the purification, and the labour of removal from the purifier avoided, by the admission of 2 per cent. of air into the gas before it enters the purifiers; this, however, is objectionable as introducing the diluent nitrogen; Valon's process substitutes oxygen (0·5 per cent.) for the air.

The spent oxide is valued in this country for its sulphur, which is recovered by burning it in the manner of pyrites "smalls" (see *Sulphuric acid*, Vol. II., p. 5). As the hydrated ferric oxide also removes HCN and HSCN it is, when spent, valued chiefly on the Continent for the Prussian blue and sulphocyanides which it is capable of yielding (see *Cyanide*, Vol. II., Chap. XVIII.).

The lime also removes the CO_2, together with a portion of the H_2S and the CS_2, in the following manner:—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$Ca(OH)_2 + 2H_2S = Ca(SH)_2 + 2H_2O$$
$$Ca(OH)_2 + H_2S = Ca(SH)(OH) + H_2O$$
$$Ca(SH)_2 + CS_2 = CaCS_3 + H_2S$$

The sulphur is not recovered from the spent lime, which is sometimes reburnt with the elimination of most of the sulphur as SO_2, and of all the CO_2, but with the simultaneous formation of a good deal of calcium sulphate, the accumulation of which soon renders fresh lime necessary.

The best arrangement for combining the advantages of these three purifying materials is as follows:—Each is disposed on wooden trays arranged in tiers in an iron box, L, provided with a cover, having a water seal to allow of its ready removal. The gas is forced by the above-mentioned exhausters through a series of these in the following order:—The first ("carbonate vessel") contains moist slaked lime, and chiefly removes CO_2; it is incapable of removing much of the H_2S, because of the decomposing effect of the CO_2 on the calcium hydrosulphide which would be formed. The second ("oxide vessel") is filled with the hydrated ferric oxide, generally Irish bog ore containing about 32 per cent. of $Fe_2O_3.H_2O$, finely ground and mixed with an equal bulk of sawdust; this removes most of the H_2S. The third ("sulphide vessel") contains the slaked lime from an earlier purifier which has become saturated with H_2S, and is rich in calcium hydrosulphide; this removes most of the CS_2, and the sulphur content of the gas is thereby lowered to a point such as that adopted as a standard by the Metropolitan Gas Referees. The last ("check vessel") contains moist slaked lime or ferric oxide, and removes the remaining trace of H_2S which has been expelled from the calcium hydrosulphide by the CS_2. These purifiers are generally worked in pairs.

The use of Weldon mud (see *Alkali*, Vol. II., p. 38) has been recently adopted. The chemistry of its action on the H_2S is similar to that of the action of Fe_2O_3 (*v.s.*), but traces of H_2S are more easily removed by it than by ferric oxide. Weldon mud is easily revivified *in situ* by the admission, together with the coal gas, of a volume of air appropriate to the percentage of H_2S to be removed; about 1 per cent. of the volume of the gas is generally sufficient, if the vessel be periodically blown through with pure air.

The gas issuing from the purifiers is measured by passing through the station metre, M, and is collected in the gasholder, N. The pressure of the gasholder is usually sufficient to effect the distribution of the gas through the mains unless the consumers be at considerable distances, when additional pumps on the principle of the Beale's exhauster are necessary for this purpose.

Products—Gas.—According to Mills the average yield of the chief products for large works per 100 parts of coal is—gas (specific gravity 0·48, 17 candle power) 16·6 per cent., ammoniacal liquor 14·1 per cent. (yielding $(NH_4)_2SO_4$, 0·87 per cent.), tar 5·3 per cent., coke 66 per cent.

The following table gives the average composition of the gas before and after purification :—

	Unpurified.	Purified.
	By vol.	By vol.
H,	47 per cent.	51 per cent.
CH_4,	34 ,,	36 ,,
CO,	5 ,,	5 ,,
Heavy hydrocarbons (C_nH_m),	4 ,,	4 ,,
H_2S,	1 ,,	...
NH_3,	1 ,,	...
CO_2,	4 ,,	...
N,	4 ,,	4 per cent.

The constituents of the crude gas, which are commonly called impurities, are generally quoted in terms of grains per 100 cubic feet. Thus, Butterfield * gives the following table as expressing the limits for Durham coal carbonised at moderately high temperature :—

			Grains per 100 cubic feet.
Ammonia,	0·65 to 0·95	per cent. by vol.	or 200 to 300
Carbonic acid,	1·2 ,, 1·8	,, ,,	980 ,, 1,470
Sulphuretted hydrogen,	0·9 ,, 1·5	,, ,,	570 ,, 950
Carbon bisulphide,	0·020 ,, 0·035	,, ,,	28 ,, 50
Other sulphur compounds,	... ...		5 ,, 8
Cyanogen,	0·05 ,, 0·10	,, ,,	50 ,, 100

* *Gas Manufacture* (Chas. Griffin & Co., Ltd.).

The manner in which the composition and quality of the gas are influenced by the temperature of distillation is illustrated below (*L. T. Wright*). Newcastle coal yielded at the temperatures named :—

	Dark red heat.	Bright red heat.	Bright orange heat.*
Cubic feet of gas per ton, .	8,250	9,692	12,006
Illuminating power of equal vols. of gas (candles), . .	20·5	17·8	15·6
Illuminating power (candles) of gas from equal weights coal, ...	34	35	37
Hydrogen (H) per cent., .	38·1	43·8	48·0
Methane (CH_4), . . .	42·7	34·5	30·7
Carbon monoxide (CO), . .	8·7	12·5	14·0
Heavy hydrocarbons (C_nH_m),	7·6	5·8	4·5
Nitrogen (N), . . .	2·9	3·4	2·8

The gas in these experiments was lime-purified. It will be seen that although the gas made at the higher temperatures is poorer in illuminating power when equal volumes are compared, yet that the total illuminating power obtained from the greater volume of gas given off at high temperatures of carbonisation is in excess of that yielded by the gas produced at low temperatures.

In modern practice the greatest possible yield of gas is obtained by carbonising at high temperatures, and the illuminating power is brought up to the standard (*v.i.*) by enrichment, which is dealt with in later paragraphs. It is to be noted that a high temperature of distillation increases the quantity of the chief impurities, CO_2, H_2S, CS_2, and CN. Thus, in certain results it was found that the CO_2 varied between 16 and 18 grains per cubic foot; the H_2S between 8·4 and 10·6 grains per cubic foot; the CS_2, 0·27 and 0·40, and the CN, 0·13 and 0·56 grain per cubic foot.

Valuation and Utilisation of Coal Gas.—The valuation of gas for commercial purposes generally consists in the determination of its illuminating power and the estimation of its objectionable impurities. The illuminating power is measured by a photometer, the standard instrument prescribed by the Gas Referees being the "Evans." Its principle consists in illuminating a paper which is greased, save for a central spot; one side of this paper is illuminated by the gas to be tested, burnt at the rate of 5 cubic feet per hour from a standard burner, and on the other by the standard light which is obtained from one or two sperm candles (six to the pound), each burning at the rate of 120 grs. per hour. The position of

* For the temperatures roughly equivalent to these technical phrases see Vol. I., p. 83.

the screen between the two lights, when the non-greased spot appears similar to the greased part of the paper on viewing it from both sides, serves to measure the illuminating effect of the two lights, their intensities varying directly as the square of their distance from the screen. (A more accurate standard light has been devised by Vernon Harcourt, and consists of a burner consuming a mixture of air and the vapour of the hydrocarbon pentane, C_5H_{12}, giving the light of one sperm candle. At present the instrument has been considered too delicate for practical use.*) The illuminating value, however obtained, is expressed as the number of standard candles to which it is equivalent. This value is roughly judged at the gas works by ascertaining what pressure is required to yield a flame 7 inches in height, from a standard jet (jet photometer); this depends on the fact that the amount of gas issuing from a constant orifice, at constant pressure, is dependent upon its specific gravity, which is roughly related to its illuminating power; thus, 16-candle gas is about specific gravity 0·36 to 0·38; 19-candle gas, 0·42 to 0·43; 20-candle gas, 0·45 to 0·46; gas from Boghead cannel (36-candle), 0·75. The lower the specific gravity of the gas, and the lower its illuminating power, the higher the pressure needed to give a 7-inch flame.

With regard to the objectionable impurities in gas, the sulphur compounds are injurious in that SO_2 is produced by their combustion, and some sulphuric acid is ultimately formed. The ammonia is objectionable from its tendency to form cyanogen and oxides of nitrogen during combustion. H_2S is tested for, separately from the other sulphur compounds, by exposure of paper soaked in lead acetate to a stream of the gas (10 cubic feet in all, per test); it should be entirely absent, as shown by the paper remaining undarkened. An ingenious instrument has been devised for obtaining a continuous record of the freedom, or otherwise, of the gas from H_2S, and consists of a strip of lead paper caused to traverse a bell jar through which the gas is passed, the paper being driven by clockwork at a known rate, and entering and leaving the jar by mercury traps.

The ammonia is next determined by passing the gas through a glass cylinder filled with beads moistened with a solution containing a known quantity of sulphuric acid; from the amount of this remaining unneutralised after the experiment, the quantity of ammonia is calculated. In the Metropolis its amount must not exceed 4 grains per 100 cubic feet. For determining the sulphur compounds, other than H_2S, the gas is finally burnt in a Bunsen burner and the products of combustion caused to pass up a tower filled with glass marbles. The air in which the gas burns is drawn through lumps of ammonium carbonate, the vapour of which fixes the SO_2, ammonium sulphite and sulphate

* Another instrument (the Dibdin lamp) on the same principle has been devised, which is free from this objection.

being produced; these are caught by the water of combustion and condensed by the cold glass marbles. The water is collected, and the sulphur in it determined as barium sulphate. The sulphur must not exceed 17 grains per 100 cubic feet in summer, and 22 in winter.

The illuminating power of coal gas doubtless depends on the nature and quantities of its constituents, but the relation between the two is not yet thoroughly ascertained.

It is customary to consider the constituents as falling into three classes:—(1) The illuminants; (2) the non-illuminant combustible gases; (3) the diluents which contribute neither to the luminous nor to the heating effect. The illuminating effect is generally agreed to be ultimately due to the separation of solid carbon in the flame, though the reactions by which this is brought about are still under discussion. Formerly it was supposed that the unsaturated hydrocarbons, which consist mainly of members of the olefine, acetylene, and benzene series, were alone concerned in the production of light, inasmuch as these bodies are known to burn with luminous flames. At the present time there is reason to believe that the chief saturated hydrocarbon present—viz., CH_4—which by itself has a non-luminous flame, yet when heated to the temperature of a coal gas flame will also contribute to the luminosity by its decomposition, so that the former criterion known as "carbon density," by which term was implied the ratio of carbon to hydrogen in the unsaturated hydrocarbons, is of doubtful value. Hydrogen and carbon monoxide are the chief non-illuminant combustible gases, and serve to raise the temperature of the flame, upon which the incandescence of the carbon depends. Nitrogen and carbon dioxide are the main diluents, and diminish the luminosity of the flame by absorbing heat, and by increasing the volume of the flame. The proximate composition of an average sample of coal gas (South Metropolitan) is, according to V. B. Lewes,

	Per cent.
Hydrogen,	57·08
*Unsaturated hydrocarbons,	4·38
Saturated ,,	33·99
Carbon monoxide,	2·63
,, dioxide,	0·79
Nitrogen,	0·96
Oxygen,	0·15
Carbon bisulphide,	0·02

Inasmuch as the illuminating power of gas depends largely upon the conditions of combustion, as distinct from the composition of the gas itself, much attention has been paid to the form of burner which shall combine the highest illuminating effect with the smallest consumption of gas. There are four types of burners in general use:—(1) The simple jet so arranged as to spread the

* Containing acetylene, 0·035.

flame in a broad thin sheet, with or without a regulating valve for governing pressure—*e.g.*, the common "batswing" and "fishtail." (2) The argand, in which a greater supply of air is obtained by means of a glass chimney surrounding an annular flame, the temperature of which is raised by the heat radiated from one side of the ring to the other. (3) The regenerative burner, in which the gas is burnt in a ring and the products of combustion are caused to circulate round the air supply, and thus heat it; such are the Wenham, Siemens, and Fourners. (4) The incandescent burner, such as the Welsbach, in which an air-gas flame (*v.i.*) plays upon refractory material, in the form of a cap or mantle, and heats it to incandescence.

The air-gas flame is produced by allowing the gas to stream from a small orifice, whereby it produces a lowering of pressure in its immediate neighbourhood, and draws in a supply of air (about two and a-half times its volume), with which it mixes as it passes up a wide tube, burning at the end of this tube with a flame which is rendered non-luminous, partly by the diluting action of the air, and partly by the presence of sufficient oxygen to burn the hydrocarbons without the intermediate liberation of carbon. The advantages of this flame are that it is hotter in certain portions than a similar luminous flame, and that it does not deposit soot. If arrangements be made to admit more air than two and a-half times the volume of the gas, the flame becomes smaller and burns with a greenish inner cone, and is much hotter, inasmuch as the action of excess of oxygen overcomes the diluting effect of the air. Such burners are known as "solid flame burners," and must be provided with a metal gauze cap to prevent the explosive mixture of gas and air taking fire down the tube. The action of the gauze is similar to that in a Davy safety-lamp, and depends upon the fact that if the heat of a flame be rapidly conducted away, the flame is extinguished. A quiescent mixture of gas and air is only explosive when the quantity of gas lies between 5 and 30 per cent. of the total volume of the mixture. Burners of this description are used for gas fires and cooking stoves.

The relative illuminating power of gas burnt under different conditions is shown by the following table (*A. Wilson*):—

	Candle Power per Cubic Foot per Hour.	British Thermal Units per Candle Power per Hour.
Flat flame, . . .	2	347
Argand, ...	2·2	315
Siemens regenerative, .	2·6	266
Wenham, ...	4·5	154
Welsbach, . . .	7·0	99

From this it is seen that, apart from other considerations, such as first cost and cost of maintenance, the incandescent system is the most economical.

The conversion of the chemical energy of coal gas into light is extremely imperfect, only about 0·5 per cent. of the total energy appearing as luminous vibrations in the case of a common argand. Regenerative burners have about double this efficiency—viz., 1 per cent. The quantity of energy appearing as luminous radiation from an incandescent electric lamp supplied by a gas engine and dynamo is about 0·75 per cent. of the chemical energy of the gas consumed in the engine, while if an arc light be used the efficiency rises to 3·5 per cent.

For the utilisation of coal gas for domestic heating and as a source of mechanical power, see Vol. I., p. 61.

Enrichment of the Gas.—This was, until recently, wholly effected (when done at all) by carbonising sufficient cannel coal to bring the illuminating power to the required standard. The quantity generally used is about 10 to 15 per cent. of the coal carbonised. The cannel is mixed with the ordinary gas coal, and the two carbonised together. The name "cannel" is from the word "candle," the analogy arising from the fact that a splinter of the coal burns brilliantly when ignited. Cannel is of the nature of a shale rather than of a true coal, and its composition (p. 57) indicates the divergence, which is also illustrated by the quality of the tar obtained during the distillation. This contains so much paraffin that it is of little value to the tar distiller. (Compare *Shale*, Vol. II., p. 100). The candle power of cannel gas varies according to the quality of the cannel and the temperature of distillation, but is usually as high as 30 c.p. The following analyses of gas supplied to Scotch towns are given by P. Frankland :—

	Illuminating Power.	Unsaturated Hydrocarbons.	Saturated Hydrocarbons.	H.	CO.	CO_2.	O.	N.
Edinburgh,	30	12·23	42·93	33·24	6·61	0·35	1·00	3·64
Glasgow,	27	10·00	40·26	39·18	7·14	0·29	0·06	3·07
St. Andrews,	27	10·04	42·13	33·63	5·16	2·73	0·48	2·83

From these it will be seen that the unsaturated hydrocarbons, or "illuminants," are present in more than twice the quantity found in ordinary coal gas, and that the saturated hydrocarbons are also considerably higher, while the hydrogen shows a corresponding decrease. The difference of illuminating power is dependent upon these facts.

The increasing dearness and badness of cannel have led to the

use of other methods of enriching gas. That at present most in use consists in adding a regulated amount of water gas, charged with the vapours of comparatively heavy hydrocarbons, to the gas produced in the retorts from common gas coal.

Water gas is the product of the action of steam upon heated carbonaceous fuel, the fundamental reaction governing its formation being $H_2O + C = CO + H_2$.

This reaction is endothermic—*i.e.*, it requires the application of extraneous heat to maintain it. The amount of heat that has to be supplied is 38,770 gram-units per 18 grams of liquid water decomposed. The heat necessary to produce the decomposition may be supplied by heating the vessel containing the carbonaceous matter (generally coke) in a furnace, but such procedure is uneconomical and the usual practice is to bring the coke to a white heat by means of the exothermic reaction—$C + O + N_4 = CO + N_4 + 29{,}690$ gram-units per 12 grams of C burnt. The method adopted for taking advantage of both these reactions is as follows:—The fuel is contained in a firebrick chamber (the *producer* or *generator*), at the bottom of which a blast of air is delivered at 12 to 15 inches water pressure. The resulting producer gas (CO and N) is led into another firebrick vessel or "stack" packed with brickwork where it meets a fresh supply of air and is partially burnt, heating the brickwork to whiteness; the partially burnt gas then passes into another similar stack where it meets a second supply of air and is completely burnt, thus furnishing a second hot chamber. At the end of about five minutes the blast of air is shut off and steam, at about 130 lbs. per square inch, let in through the heated coke producing water gas, an example of the average composition of which is—H 49·17, CH_4 0·31, CO 43·55, CO_2 2·71, N 4·06, H_2S 0·2.

After it has left the coke, the water gas passes into the first brickwork chamber (*carburettor*) where petroleum oil (which may be fairly crude, but must be free from cokey residue when distilled), such as "solar oil"—a product from the distillation of Russian petroleum, intermediate between the burning and lubricating oils (see *Petroleum*, p. 122), of specific gravity 0·87—is sprayed in, and then into the second chamber (*superheater*) where the oil which has been already vaporised and partly decomposed or "cracked" is "fixed"—*i.e.*, resolved into more nearly permanent gases. This enriched water gas is then scrubbed, passed through purifiers, and mixed with the purified coal gas from the carbonising retorts. The benefit to the coal gas will be gathered from the following analysis of a sample of New York oil-water gas:—H 26·25, saturated hydrocarbons 28·91, CO 27·12, N 1·92, unsaturated hydrocarbons 15·80, candle power 29·68. The character of the unsaturated hydrocarbons produced during the cracking and fixing is but little known;

there seems reason to suppose, however, that they are relatively rich in benzene.

If the gas coke be used for making water gas, 1 ton of coal could first be made to yield 12,000 cubic feet of coal gas, and the resulting coke (about 60 per cent. of the weight of the coal) could produce about 18,000 cubic feet of water gas and 66,000 cubic feet of producer gas. The respective fractions of the total energy of the coal thus represented are best compared as follows:—

	Cu. ft. × Cal.	Cal.
Coal gas, ...	12,000 × 170	2,040,000
Water gas, ...	18,000 × 74	1,332,000
Producer gas, ...	66,000 × 28	1,848,000
		5,220,000

Taking the coal as having a calorific value of 8,300 Cal.—*i.e.*, yielding 8,300,000 Cal. per ton of 1,000 kilos.—this is equivalent to an efficiency of 63 per cent. It will be noted that the heat required to distil the coal destructively must be deducted if the net efficiency of the process has to be reckoned. The cost of carburetted water gas is not very different from that of coal gas, its advantages lying less in cheapness that in ease of control and adaptation to the maintaining of the illuminating value of the coal gas with which it is mixed. It has a special value in countries containing anthracite but little bituminous coal, as by this means the former can be used for the production of lighting gas by conversion into water gas and subsequent enrichment of the product.

Other methods of enriching gas, depending on the introduction of the vapour of hydrocarbons less costly than benzene, into the coal gas, have proved more difficult of application owing to the tendency of the vapours to deposit in the delivery pipes. Nevertheless, considerable success has attended the use of the system in which a light petroleum oil (*carburine*, specific gravity 0·68) is passed through steam-heated pipes, and the vapour is admixed with the gas. One gallon of such oil will impart 1 candle power to 8,000 cubic feet of gas. The cheapening of benzene by its recovery from coke ovens (*q.v.*) has led to its proposed use for enrichment.

Another system of the same class is that known as the "albocarbon," in which the gas passes over melted naphthalene heated by the burner itself. All these methods of enrichment entail the consumption of the gas immediately after the enriching vapour has been introduced.

It has recently been found possible to manufacture *calcium carbide* (CaC_2) by heating a mixture of chalk and coke in an

electric furnace. This compound evolves *acetylene* (C_2H_2) when brought in contact with water—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

Acetylene, being an endothermic compound (C_2, H_2 = −47,750 gram-units), and capable of easy decomposition with separation of carbon, burns with a flame which is of high temperature and high illuminating value (240 candles per 5 cubic feet per hour). It appears, however, that the value of this gas as an illuminant is much depreciated when the gas is mixed with coal gas, so that the "enrichment value" of acetylene is comparatively poor. Acetylene will probably come into use as an illuminant on a small scale; it is liquefied by a pressure of about 80 atmospheres at 18° C. = 64° F.; the liquid is colourless, and has a specific gravity of 0·4. Water at 18° C. = 64° F. dissolves about its own volume of the gas. Commercial calcium carbide contains about 80 per cent. of CaC_2, and yields some 10,000 cubic feet of acetylene per ton. The gas has a considerable action on copper and brass.

Another method of enrichment consists in converting a portion of the tar into gas. This is effected in the Dinsmore process by allowing the gas, direct from the ordinary retorts, and, therefore, still containing its tar, to pass through an empty retort kept at a regulated temperature, whereby a portion of the tar is gasified. The use of cannel for enriching is rendered unnecessary by this plan. As a consequence of the secondary heating of the tar and gas, the former is, in both quantity and quality, inferior to ordinary gas tar, and there is also some risk of decomposing a portion of the ammonia in the gas. The process has therefore not come into extended use.

Oil Gas.—Although not used for enriching coal gas, oil gas is conveniently treated here on account of the similarity of its mode of preparation to that of the hydrocarbons used for enriching water gas (p. 72). On the Pintsch system, shale or petroleum oil is run at the rate of 12 gallons per hour from a cistern on to a sheet-iron tray contained in the upper of two O-shaped cast-iron retorts set in a furnace. It is there "cracked," and the products passed from the opposite end of the retort down into the second retort, which is the hotter. The temperature of the retorts is very high, and the operation is conducted under a pressure of 3 to 4 inches of water. The gas passes through condensers, is washed by passage through water, and is purified by a mixture of lime and sawdust before passing into the gasholder. The yield of gas is about 80 cubic feet per gallon; its candle power is about 50 to 60. The gas is rich in hydrocarbons of the olefine and benzene series, to which it owes its value as an illuminant. The sole use for oil gas in this country is in supplying lights for railway carriages

and buoys. For the former purpose it is compressed to about 10 atmospheres, and during the process deposits a liquid rich in benzene and toluene, commercially known as "hydrocarbon," in the proportion of about 1 gallon per 1,000 cubic feet. It loses illuminating power by this separation, and after compression is of about 40 to 50 candle power.

Gas Liquor.—This product is the aqueous portion of the liquor condensed in the hydraulic main and condensers, together with the water used in the scrubbers. It consists mainly of a solution of ammonium salts, a number of which are those of feeble acids, such as hydrosulphuric and carbonic acids. These salts are easily split up on boiling the liquor, so that the ammonia combined with them is termed "free ammonia." The remainder are salts of stronger acids, and can only be decomposed by an alkali stronger than ammonia, such as lime. The ammonia in this condition is called "fixed ammonia." The following analysis of a Leeds gas liquor (*Dyson*) shows the usual composition :—

	Grams per litre.
Ammonium sulphide, ...	3·03
,, monocarbonate, ...	39·16
,, chloride, ...	14·23
,, sulphocyanide, ...	1·80
,, sulphate, ...	0·19
,, hyposulphite, ...	2·80
,, ferrocyanide, ...	0·41

The volume of gas liquor to be disposed of in the works will depend on the character of the coal, the conditions of distillation, and the amount of ammonia which is permitted to remain in the purified gas, and varies greatly in different works. Coals used in London yield comparatively little liquor from the hydraulic main, but the gas has to be sent out containing not more than 4 grains of ammonia per 100 cubic feet ; a considerable quantity of water has to be used in the scrubbers to attain this end.

The varying amount of ammonia, obtained in the liquor in the hydraulic main from different coals, is shown in the following table :—

Kind of Coal.	Ammonia.	
	Fixed per cent.	Free per cent.
Silkstone, 1, . . .	1·89	0·35
,, 2, . . .	2·21	0·27
,, 3, . . .	2·27	0·47
Parkgate, . . .	2·40	0·70
Cannel, ...	1·60	0·46

The liquor from small works, in agricultural districts, is some-

times applied directly as a manure, but in large works it is used for the production of ammonium sulphate, which is also chiefly used for manurial purposes (**manure salts**), see *Artificial Manures*, Vol. II., Chapter IV. Incidentally, the sulphur present as ammonium hydrosulphide is evolved as H_2S, which is burnt in Claus kilns (see *Alkali*, Vol. II., p. 33) for the recovery of the sulphur.

The working up of the gas liquor for ammonium sulphate is carried out in the following manner:—The liquor is heated to drive off the free ammonia, and the vapour is absorbed in sulphuric acid, forming ammonium sulphate, which crystallises and is periodically fished out. It is the common practice in England to use only that part of the ammonia which is liberated on distilling the liquor alone, but sometimes, especially on the Continent, the fixed ammonia is liberated by the addition of lime. A typical apparatus is described in the section dealing with the recovery of ammonia (see *Ammonia-Soda Process*, Vol. II., p. 47).

Commercially, ammoniacal liquor is evaluated by the number of ounces (avd.) of pure oil of vitriol required to saturate 1 gallon of the liquor. The common strength is about 8 ounces.

Coal Tar.—Coal tar may be considered as those products of the distillation which distil at a temperature above the boiling point of benzene (80° C. = 176° F.), containing in solution small proportions of more volatile products, of the same classes as those which occur in the gas itself. The condensation occurs in the hydraulic main, the condensers, and to a smaller extent in the scrubbers. The specific gravity of tar varies between 1·1 and 1·2, and is usually between 1·12 and 1·15. The influence of the temperature of distillation on the specific gravity and yield of coal tar for different kinds of coal is shown by the following table:—

Class of Coal.	Temperature of Distillation.	Specific Gravity of Tar.	Percentage Yield on Coal.
Derbyshire black shale, No. 1,	Very high,	1·210	5·74
	Normal,	1·185	...
	Very low,	1·145	5·88
Derbyshire black shale, No. 2,	Very high,	1·207	6·47
	Normal,	1·185	...
	Very low,	1·136	7·29
Notts top hard cannel, . .	Normal,	1·147	10·92
	Very low,	1·116	11·86

Tar is a very complex mixture, and contains the following classes of substances:—(1) Hydrocarbons of the paraffin and benzene series, the former in small quantities; naphthalene, anthracene, and their homologues. (2) Phenols and their con-

generers. (3) Sulphur compounds, including H_2S, CS_2, mercaptan and thiophen, present in small amount. (4) Nitrogen compounds, such as ammonia, aniline, and other organic bases. (5) Compounds of uncertain character, rich in carbon, constituting the pitch. Of these the benzene hydrocarbons, the phenols, the naphthalene, anthracene and pitch are present in largest quantity, and are separated by distillation in the following manner:—The tar is always wet with gas liquor, and is separated from this as far as possible by subsidence, as the presence of water causes frothing in the stills. The retort is a vertical cylindrical vessel with an inwardly curved bottom and a dome-shaped top through which a thermometer passes; it holds about 25 tons. It is heated by direct firing, and is fitted with steam jets at its lower part for blowing in steam towards the end of the distillation. Occasionally horizontal cylindrical stills with mechanical stirrers are used. The vapours pass from the still head to the condensers which are usually cast-iron worms cooled with water in the usual way. The products are collected in closed tanks which are changed as the different fractions, best indicated by the temperature of their distillation, come over; an outlet must be provided for permanent gases such as H_2S, CS_2, and paraffin hydrocarbons, which are evolved at various stages of the distillation, and is either connected with a chimney shaft, or, if nuisance must be avoided, with a set of scrubbers and purifiers.

The distillate is collected in the following fractions:—(1) First runnings, up to 105° C. = 221° F. (2) Light oil, up to 210° C. = 410° F. (3) Carbolic oil, up to 240° C. = 464° F. (4) Creosote oils, up to 270° C. = 518° F. (5) Anthracene oil, from 270° C. to the "pitching point," which varies according to whether hard or soft pitch is to be made. In modern practice the first two fractions are frequently collected together. Although the receiver is changed at the above-mentioned temperatures, it must be remembered that the fractions will contain compounds which boil at higher temperatures than those named, on account of the tendency of one vapour to carry over others at its boiling point, even though their boiling points be higher. The proportions of the five fractions vary greatly. The following is the typical composition of Beckton tar:—

First runnings, . .	3·66 per cent.,	consisting of ammoniacal liquor, 2·00 per cent.; crude naphtha, 1·66 per cent.
Light oils, . . .	1·62 ,,	
Carbolic and creosote oils,	15·70 ,,	
Anthracene oils, . .	20·73 ,,	containing crude anthracene (30 per cent. real anthracene), 1·90 per cent.
Pitch, ...	56·29 ,,	
Loss, ...	2·00 ,,	
	100·00	

The first runnings consist of ammoniacal liquor—which is added to, and worked up with, the main quantity previously separated by subsidence—and **crude naphtha**, which consists of hydrocarbons of the benzene series, mainly benzene and toluene, accompanied by the more volatile impurities of coal tar, such as CS_2, thiophens, &c. This is generally worked up with the light oils.

The light oil (specific gravity about 0·9) derives its name from its being lighter than water; it consists of a large number of hydrocarbons of the benzene series, among which benzene is present in minor quantity; toluene and the three xylenes occur in somewhat greater amount, together with heavier hydrocarbons. Bases of the pyridine series and tar acids or phenols are also present. The first step in working up the light oil is redistillation, which takes place in a still similar to that used in distilling the tar; the distillate is then divided into first runnings, which are similar to those obtained from tar itself and are worked up with them as described below for crude naphtha, and last runnings, which contain the phenols and are added to the carbolic oil.

The crude naphtha is first agitated successively with strong sulphuric acid and caustic soda; the former combines with the bases, dissolves part of the thiophens and olefines, and chars other impurities; the latter removes the tar acids (phenols) and neutralises residual sulphuric acid. Inasmuch as the acid also converts phenols into sulphonic acids, from which the phenols are not easily recoverable, it is preferable to treat first with caustic soda (specific gravity 1·15) to remove these, and then with sulphuric acid, finishing by washing with a weaker solution of soda. The "acid tar," as the spent acid is termed, is used for making ammonium sulphate after the separation of the coarser impurities, and as a source of pyridine bases used to denature alcohol for industrial purposes in Germany. The spent soda is acidified with sulphuric acid, and the liberated tar acids worked up with the carbolic oil. The naphtha thus purified is fractionated in a still of the same pattern as that used for the tar itself, the distillate being collected up to 140° C. = 284° F. for benzols, and from 140° to 170° C. = 338° F. for solvent naphtha. The distillate up to 140° C. is about 50 per cent. of the total, and that between 140° and 170° C. 25 per cent., the remaining 25 per cent. being heavy oil, which goes to be worked up with the carbolic oils.

The fractionation of the crude **benzol** is effected in a still heated by a steam coil, and provided with means for injecting steam towards the end of the distillation. In this and the subsequent rectifications the still is fitted with a dephlegmator—that is to say, an arrangement for condensing the less volatile products and returning them to the still; it is generally either a coil surrounded by water kept at a constant temperature, or a

tower similar to that used in the Coffey still (see *Brewing and Distilling*, Vol. II., Chap. IX.).

The benzol is mainly required by the aniline colour maker who uses two qualities—one containing some 70 per cent. of benzene and about 25 per cent. of toluene, and known in the trade as "90 per cent. benzol," meaning that this proportion of it distils below 100° C.;* the other containing about 44 to 48 per cent. of benzene and much toluene, and known as "50 per cent. benzol," meaning that this proportion of it distils below 100° C.

By regulating the temperature of the dephlegmator, either quality may be obtained, or the hydrocarbons themselves may be isolated; benzene (boiling point, 80° C. = 176° F.), toluene (boiling point, 111° C. = 232° F.), and xylene (boiling point, 138° to 141° C. = 280° to 286° F.)—a mixture of the three isomeric hydrocarbons thus known—are now articles of commerce. The purest benzene is obtained by freezing the commercial product; its melting point is 5·5° C. = 42° F.

Beside these products from the crude benzol, a portion boiling up to 170° C. = 338° F. (compare p. 78) is marketed as "solvent naphtha;" this is similar to the fraction boiling between 140° to 170° C. from the distillation already referred to, of the washed crude naphtha. Solvent naphtha consists largely of xylenes and cumenes, and is so called from its application as a solvent for indiarubber. It should be free from naphthalene, which is often present in a similar fraction used for burning in street lamps, and known, therefore, as "burning naphtha."

The **carbolic oils**, which are included with the creosote oils mentioned in the analysis of tar quoted above, amount to 4 to 5 per cent. of the original tar. The point at which the receiver of the tar still is changed, is fixed not only by the temperature, but by the appearance of solid naphthalene in the distillate, an indication that the bulk of the "tar acids"† (phenol and its homologues, commercially known as carbolic and cresylic acids) has come over. The oil is filtered from such naphthalene as separates on cooling, and is extracted with a solution of caustic soda which dissolves out the tar acids. A cheaper method is that known as the West-Knight and Gall process, which consists in treating the oil with a mixture of lime and sulphate of soda, whereby sulphate of lime and the sodium salts of the tar acids, "sodium carbolate," are formed. The un-

*In this and all other cases, "benzol" is used to signify the commercial product, while "benzene" indicates C_6H_6. Both are absolutely distinct from "benzine," which is a petroleum product. Toluol and xylol are commercially used for toluene and xylene.

†These are now sold as disinfectants, being dissolved in a soap solution for this purpose: trade names such as creolin and lysol are used for such solutions.

attacked neutral oil is sometimes worked up for naphthalene (*q.v.*), or if this be not wanted the oil is returned to the light oils, inasmuch as it contains benzene homologues. The alkaline solution of sodium carbolate is generally mixed with the alkaline washings of the light oil (*v.s.*), and treated with sulphuric acid, which sets free the tar acids, these floating upon the aqueous liquid as an oily layer. The sodium sulphate formed is practically valueless where caustic soda has been used for extracting the tar acids, but can be used over again when a mixture of sodium sulphate and lime has been employed. In any case the aqueous liquor is drawn off, the crude tar acids allowed to settle for a day or two, and sold as "crude carbolic acid" of specific gravity 1·05 to 1·065. The "crude carbolic acid" is worked up for "pure carbolic acid"—*i.e.*, phenol, $C_6H_5(OH)$.

The crude acid contains, besides phenol, cresol, water and some neutral oils. The separation of phenol and cresol is effected either by fractional distillation or fractional precipitation of their solution in caustic soda with sulphuric acid. When an insufficient quantity of acid is added to a solution containing the sodium salts of phenol and cresol, the latter, as the weaker acid, is first precipitated, and thus can be separated from the undecomposed sodium salt of phenol, which is then similarly acidified, and the phenol got out. However obtained, the fraction richest in phenol solidifies on cooling to about 10° C. = 50° F. The crystals (melting point 42° C. = 108° F., boiling point 182° C. = 360° F.) are freed from the still liquid portion by treatment in a centrifugal machine, and generally again distilled with an addition of 0·2 to 0·3 per cent. of potassium bichromate, and a little sulphuric acid; the object of the addition of this oxidising agent being to destroy the impurity that hastens the change by which even pure phenol becomes red on exposure to air and moisture; this discoloration takes place especially easily when the acid has been distilled from a metal still, so that the pharmaceutical product is finally distilled in glass. The commercial grades of carbolic acid comprise those containing water—which in consequence melt at a lower temperature than the anhydrous acid—and mixtures of phenol and cresol. In consequence, the term "carbolic acid" is objectionable because necessarily vague. The chief uses of all the grades are for disinfecting purposes, the production of salicylic acid, colouring matters, and explosives (*q.v.*).

The **creosote oils** are chiefly valuable on account of the naphthalene they contain, and for their use as a preservative for timber (see Vol. I., p. 46). They consist of a solution of naphthalene, anthracene, and similar solid hydrocarbons, in liquid hydrocarbons, the composition and nature of which have not yet been fully ascertained.

When the creosote oils, as they come from the tar still, cool,

much **naphthalene** is deposited, amounting to about 5 to 10 per cent. of the tar, and is separated by draining, and then pressed in hot presses like those used for stearic acid ("stearin") and anthracene (*q.v.*). It is further purified from acid and basic impurities by successive treatment with caustic soda and sulphuric acid. In the latter process 5 per cent. of manganese dioxide (Weldon mud; see *Alkali Manufacture*, Vol. II., p. 38) is added, in order that the final product may remain white on keeping. Some naphthalene is also obtained from the carbolic oils, as has been already mentioned. The washed naphthalene is either sublimed or distilled, preferably the latter. Iron stills heated by direct fire and provided with dephlegmators are used; a safety-valve is provided in case the worm should block, although in the best practice the "worm" is a straight pipe through the centre of which runs a small steam pipe, and round which the condensing water circulates. The portion coming over between 210° and 235° C. = 410° and 455° F. (indicated by a thermometer in the vapour) consists of nearly pure naphthalene; the object of the steam pipe in the condensing tube is to keep the naphthalene in the liquid state, and allow it to run into a receiver fitted with a partition reaching nearly, but not quite, to the bottom; through this space the naphthalene (specific gravity 1·1517, melting point 79° C. = 174° F., boiling point 218° C. = 424° F.) which sinks in the water, passes, and is collected free from water in the other division. The molten naphthalene is cast into cakes, candles or marbles, according to its intended use. The cakes are used in place of camphor as an insecticide. The candles and marbles are employed for the "albo-carbon light"—*i.e.*, for enriching coal gas with naphthalene vapour the moment before its combustion (see p. 73). Naphthalene is also converted into naphthols, nitro-naphthalenes and naphthylamines, which are used for the production of synthetic colouring matters. Nitro-naphthalene is also used for "deblooming" mineral oils—*i.e.*, removing their fluorescence—the object being to allow of their being used as adulterants without immediate detection.

The creosotes themselves after separation of naphthalene are not usually further treated, but go for creosoting timber as already described (Vol. I., p. 46). A small portion, however, is employed for the manufacture of lubricants, and also for burning in blast lamps used for outdoor illumination—*e.g.*, the Lucigen or Wells light—for which purpose it is filtered and fetches a higher price.

The **anthracene oil** or **green oil** is the last fraction of the distillate from tar, and comes over between 270° C. = 518° F. and the pitching point. The crude oil has a greenish colour, and partially sets on cooling to a buttery mass containing about 30 per cent. of solid constituents—one-third of which is anthracene, the rest being other solid hydrocarbons—*e.g.*, phenanthrene and chrysene—the remaining liquid consisting of oils of high boiling

point, of which but little exact knowledge exists. The pure anthracene does not usually amount to more than 0·7 per cent. reckoned on the original tar. Anthracene oil is worked up by allowing it to cool for a few days so that crystallisation may be as perfect as possible, and the solids are separated by means of filtration under pressure through convas bags, or by a filter press, or by a centrifugal machine. A portion of the solids remaining in the oil is recovered by redistilling and filtering again. The crude anthracene is subjected to hydraulic pressure at a temperature of about 40° C. = 104° F. The expressed oils from both operations are returned to the creosote oil tank. The pressed anthracene contains about 30 to 33 per cent. of actual anthracene, and is ground and washed with solvents, generally solvent naphtha (*v.s.*) or sometimes petroleum spirit (see *Petroleum*, Vol. II., Chap. V.), the operation being conducted in closed vessels provided with stirrers, and the solvent, after having been run off, recovered by distillation. This raises the percentage of anthracene to upwards of 50 per cent. A further purification must be effected before the anthracene can be converted into anthraquinone (its chief commercial derivative; see *Colouring Matters*, Vol. II., Chap. XIII.), by sublimation in a current of superheated steam, which gives a product containing about 60 per cent. of anthracene in a state of division sufficiently fine to allow of its subsequent oxidation to anthraquinone.] The tar distiller generally puts 30 per cent. anthracene on the market, and it is valued by the "unit"—that is, at so much per cwt. for every per cent. of anthracene present. Pure anthracene is a white crystalline substance with a bluish fluorescence; it melts at 213° C. = 415° F., and boils slightly above 360° C. = 680° F.

Pitch.—The "pitching point" varies from 360° to 400° C. = 680° to 752° F., according to the amount of anthracene oil distilled off and the quality of the pitch left. As anthracene is a valuable product, it is now customary to push the distillation so as to obtain as much of this as possible, and consequently "hard pitch" is produced. When the distillation is not carried so far, "soft pitch" results. It is blacker and more lustrous than hard pitch, and, containing a large proportion of oil, softens at 40° C. = 104° F., and melts at 60° C. = 140° F., as against 80° C. = 176° F., and 120° C. = 248° F. for hard pitch. Nowadays, hard pitch is generally softened by the addition of creosote oil, and is substituted for the old "asphalt" which was produced by stopping the distillation of tar when only light oil had been distilled off. Hard pitch contains, per cent., C, 75; H, 8; O, 16, and a trace of ash. It is used for making patent fuel (coal-dust briquettes), rough varnishes, and for adulterating natural mineral asphalt. It is sometimes distilled for a further portion of anthracene which is much contaminated with chrysene.

Gas Coke.—As already stated, a portion of this is used for

heating the retorts; the remainder finds application in the neighbourhood for such industries as cement making and lime burning, and for domestic heating. Good gas coke should not contain more than 10 per cent. of ash.

(B.) **CARBONISING IN OVENS FOR COKE PRODUCTION.**—In order to overcome objections that exist to the use of coal in many metallurgical processes (see *Iron*, Vol. I., p. 133), coke is prepared, coal being carbonised for this purpose in much larger quantities than for gas making; the essential difference in the two methods is that in the first the coke is the main product, while in the second (gas making) it is the bye-product. Gas coke cannot be substituted for oven coke on account of its lighter and more porous structure, due in great measure to the rapidity of the carbonisation. Caking coals are those best fitted for coking, because they leave a compact, coherent coke, but mixtures of caking and non-caking coals can also be successfully carbonised. As sulphur and ash are objectionable for the metallurgical use of coke, it is advantageous to use as pure a coal as possible. To this end the mineral matter (shale and "brasses"—iron pyrites) is removed by "washing." Coal-washing machinery, such as the Lührig-Coppée plant, consists essentially of sizing and levigating apparatus like that used for concentrating ores (see *Metallurgy*, Vol. I., p. 210), and by its means pure small coal can be prepared which yields good coke, which, notwithstanding that the coal used was small, will be in large pieces owing to the fusion and agglomeration that coking coal undergoes. A typical coke of good quality has the composition—C, 93·15 per cent.; H, 0·72 per cent.; N, 1·28 per cent.; O, 0·90 per cent.; ash, 3·95 per cent. The chief variation in the composition of coke is due to its content of ash, which is obviously dependent on that in the coal. For the discussion of the influence of the physical properties of coke on its suitability for metallurgical use, see *Iron*, Vol. I., p. 133.

(1) **Coking in Heaps.**—The earliest method of coking, and one which is still used to some extent, consists in carbonising coal in meilers or heaps similar to those used for carbonising wood in charcoal burning. The process is one of destructive distillation, the combustion of a portion of the coal sufficing to distil the rest, and is, therefore, analogous to coking in an oven, although there are no confining walls. The methods most in use may be reduced to three types:—(*a*) The coal is made into heaps of 20 feet diameter and 4 feet in height, or into ridges about 200 feet in length and 12 feet across and about 2 feet high, which are ignited at numerous points on the outside by driving in stakes and inserting live coal in the holes thus formed. On the cessation of the evolution of thick smoke and flame at any point, the heap at that spot is covered with coal dust and the combustion checked, and this process is pursued until the whole heap is carbonised. The main objection to this process is that the outer

part of the heap is apt to be burnt before the inner is completely carbonised. This has given rise to the use of type (*b*), which consists of a heap covered with small coal and provided with a conical brick chimney having numerous apertures. The heap is lighted by throwing burning coal down the chimney, and the combustion thus extends from the centre towards the circumference, the products of combustion escaping through the chimney, which is closed when they cease to be evolved. Type (*c*) is of similar construction, but is not covered, and the chimney is closed immediately after ignition, so that the flames proceed outwards. A variation of coking in heaps consists of coking in kilns, which are large rectangular enclosures of firebrick, with openings in the walls for the exit of gases. In coking in heaps the operation takes from two to three days, while a similar period must elapse to allow the coke to cool.

(2) **Coking in Beehive Ovens by Partial Combustion.**—This method is similar in principle to coking in heaps, in that

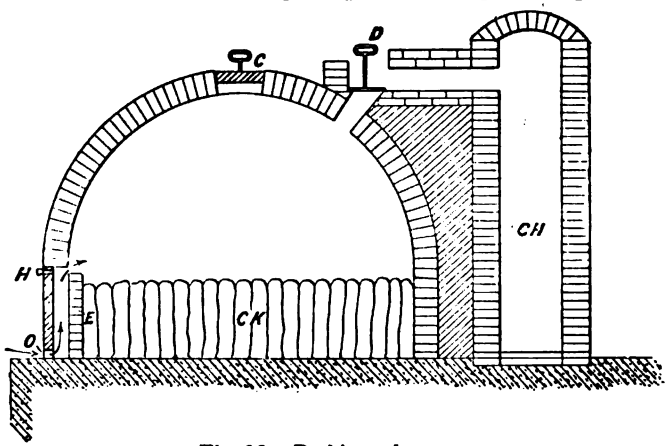


Fig. 16.—Beehive coke oven.

C, Opening for charge; O, H, air holes; C H, flue; D, damper; C K, coke; E, false door.

sufficient air is admitted into the oven to burn part of the coal and produce heat enough to carbonise the rest. As its name implies, this form of oven (one variety of which is shown in Fig. 16) consists of a dome-shaped chamber which is about 10 feet in diameter and 4 feet to the springing of the dome. The floor of the oven is traversed by a winding flue designed to keep the floor cool by the circulation of air through it, and thus prevent the rapid distillation of the fresh charge and consequent formation of bad coke. Similar flues are sometimes used for the walls. The charge for each oven is about 3 tons, which is intro-

duced either through a door in the side of the oven or through an opening in the top, C. It is held in place by a false door, E. The door is provided with holes for the admission of air, O, H. These are gradually closed after about three hours, and after some twenty-four hours are completely closed, the oven being eventually drawn forty-eight hours after charging. The smoke is led off by a flue, C H, common to a group of ovens; each oven is provided with a damper, D. If the oven be made with the whole of one side serving as a door, the coke, K, can be removed by an "anchor," which is an iron framework to which a chain can be attached, and which is inserted before the charge. In this type of oven, as in the heaps, no use is made of any of the products of distillation, the only valuable material obtained being coke.

(3) **Coking in Ovens by the Combustion of the whole of the evolved Gases.**—Ovens other than the beehive may be looked upon as enlarged gas retorts, which in most cases are set horizontally, but sometimes—*e.g.*, in the Appolt—are placed vertically. The analogy is imperfect in the present class, as the products of distillation are allowed to escape by the pressure of their evolution through holes in the walls of the retort, so that they can be mixed with the air in the surrounding flues and there burnt to supply the heat necessary for distillation. In class (4), to be described below, the analogy is stronger, as the gases are led away from the coke, and may even be used for lighting purposes.

This third type is best represented in the Coppée and the Appolt ovens, which depend upon the same principle of heating, but are somewhat different in construction. The Coppée ovens are about 2 feet wide, 30 to 35 feet long, and 4 to 5 feet to the springing of the roof. They are slightly tapered in the direction of the length for convenience of removing the coke by the thrust of an hydraulic ram. They are charged from the top, and hold from 3 to 6 tons. They are built in stacks side by side, one side of the oven being perforated, the openings leading into flues, the other side of which is in contact with the unperforated wall of the next oven. There is no recovery of products from this type of oven. The other example to be mentioned is the Appolt coke oven, in which the retort is vertical, and is about 13 feet in height, and tapering from the top 3 feet 8 inches by 13 inches to the base which is 4 feet by 18 inches. It is loaded from the top, and at the end of the run the coke withdrawn through a door at the bottom.

(4) **Coking in Ovens with Recovery of Products.**—An ideal coke oven would have the whole of the tar and ammonia recovered, and be heated exclusively by its own combustible gases. It is found, however, that as the evolution of gas slackens towards the end of the operation, the coke is insufficiently heated

and suffers in quality. It is, therefore, customary to allow either access of air to the coke towards the end of carbonisation, or to

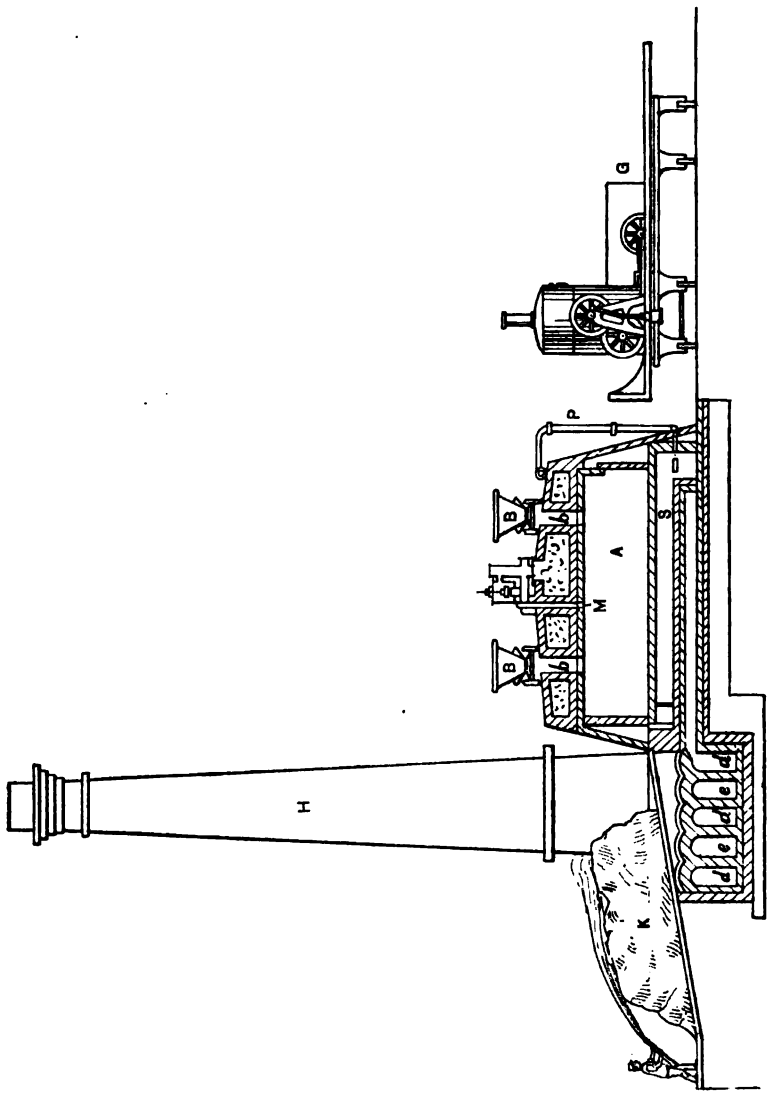


Fig. 17.—Simon-Carvès oven.

A, Oven; *b*, *b*, openings for charge; B, B, trucks; M, ascension pipe; P, pipe; S, flue; *d*, *d*, *d*, regenerating flues; *e*, *e*, flues; H, stack; G, ram; K, mode of quenching the coke.

use a supplementary mode of heating by solid fuel or producer gas.

The removal of the tar and ammonia is aided by drawing

them off by means of an exhauster, such as Beale's (see *Gas Manufacture*, Vol. II., p. 62), or by a steam injector. A well-known example of an oven for the recovery of products is the Simon-Carvès, which is very similar in construction to the Coppée oven. Fig. 17 shows the arrangement of the Simon-Carvès oven.

The oven, A, is fed through the openings, *b*, *b*, from the trucks, B, B, the gases evolved being drawn off through the ascension pipe, M, into an hydraulic main. A portion of the gas passes through the pipe, P, into the flue, S, where it meets a supply of air drawn through the regenerating flues, *d*, *d*, *d*, the products of combustion escaping through the flues, *e*, *e*, to the stack, H, which serves for a number of ovens. The coke is expelled from the oven *en masse* by the ram, G, and is quenched as shown at K.

The tar and ammonia are separated in a manner similar to that in use for the corresponding products obtained in the distillation of coal for gas production. The tar is, however, different in character from ordinary coal tar, if air be admitted to the coke. In that case it is poor in hydrocarbons of the benzene series, and consists largely of paraffins. If on the contrary no air be admitted the tar is similar to London gas tar, but poorer in light oils and phenols than are country tars. The admission of air also causes loss of ammonia by oxidation, and, in short, the improvement of the quality of the coke is effected at the expense of the other products. In the Simon-Carvès plant the yield of coke may be taken at about 77 per cent., the tar 6·12 gallons, and the ammoniacal liquor (6·7° Twaddle) 27·7 gallons per ton of coal carbonised, corresponding with 11 to 14 per cent. of the nitrogen in the coal. The tar is generally sent to the distiller, but the ammonia is worked up on the spot, in a manner similar to that used for the ammoniacal liquor of gas works. Notwithstanding the many improvements in coke ovens fitted for the recovery of the tar and ammonia, and the undoubted value of these products, and in spite of the greater yield of coke (77 per cent. as against 65 per cent.), many ironmasters prefer the coke from the old-fashioned beehive oven. The hardness and density of the coke are increased the narrower the oven—*i.e.*, the greater the opposition to the expansion of the coal while in the plastic state.

Carbonising Peat.—Attempts have been made to carbonise peat profitably in order to obtain peat charcoal, acetic acid, ammonia, and paraffin wax and oils. The process has been conducted in retorts of the modern type used for shale distillation (*q.v.*). Recent experiments show a yield from the air-dried peat of about 37 per cent. of charcoal containing about 5 per cent. of ash,* 41 per cent. of liquor containing nearly 6 per cent. of tar and a little ammonia and acetic acid, and 22 per cent. of gas

* The average from unselected samples is probably considerably higher.

containing combustible constituents. The difficulty in utilising peat in this manner arises from the fact that it occurs in a very moist and bulky condition, associated with much earthy matter, its composition being very irregular. Some preliminary process of compression and desiccation is necessary before distillation is practicable. At the present price of other carbonaceous materials (coal and petroleum) the prospect of the remunerative distillation of peat is remote.

II. DESTRUCTIVE DISTILLATION OF WOOD.

The essential constituent of wood is ligno-cellulose, which is a carbohydrate of the formula $C_{12}H_{18}O_9$. With it are associated incrusting substances consisting of resins and tannins peculiar to each species of wood. Air-dried wood contains 15 to 25 per cent. of water, while the amount of water in growing wood

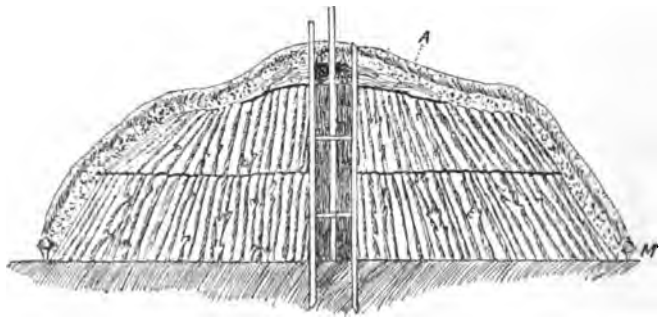


Fig. 18.—Charcoal burning in heaps. A, Covering; M, annular gap.

varies greatly with the species, ranging from 18 to 50 per cent. The ash or mineral constituents of wood amount to 1 to 1·6 per cent. The chief substances present in the ash are potassium and sodium carbonates—one or other preponderating, according to the species—lime and magnesia. The composition of the ash varies to some extent with the soil on which the trees are grown. The ultimate composition of wood (deducting the ash and moisture) averages—C, 50·5 per cent.; H, 6·3 per cent.; O, 42 per cent.; N, 1·2 per cent. When wood is heated out of contact with air, it suffers decomposition in accordance with the principles of destructive distillation detailed at the beginning of this chapter.

(A.) **BURNING IN HEAPS OR "MEILERS."**—This process is similar to that already described for coal, being indeed its prototype. The whole arrangement is shown in Fig. 18. A stake or "quandel" is driven into the ground, and around it logs of wood are carefully packed, sometimes horizontally, sometimes vertically disposed. In the latter case, three or four

stakes are used for the centre to form a sort of rough chimney. The diameter of the mound varies from 10 to 60 feet. The interstices of the logs are filled with small wood, and a covering, A, of turf or "charcoal breeze"—*i.e.*, powdered charcoal from a previous operation—is made, and is thickest at the top of the mound. The foot of the heap is not covered at the beginning of the burning, an annular gap, M, being left, the covering being supported by twigs pegged down by forks of wood, the whole arrangement being called the "armour." A channel, left during building, from the circumference to the centre of the heap, serves for the introduction of live charcoal for igniting the heap. If a chimney has been made in the middle, this serves the same purpose. The faggots immediately around the stake have been partially charred in a previous operation, so that the ignition of the heap may be ensured. When the heap is lighted, the holes are closed, and "sweating"—*i.e.*, the escape of moisture from the annular space at the base—sets in. The supply of air is regulated by partially closing the uncovered space, to avoid danger of explosion of mixtures of air and the inflammable gases that are given off. When the smoke, which is at first yellow, changes to grey, charring proper is known to have set in, and all openings are closed. During carbonisation the cover has to be renewed as it falls in. After some days a stake is driven through the covering in several places near the ground, to form passages for the escape of the tar. More perforations are made in the upper part of the heap as the charring proceeds—the judgment of the burner being guided by the appearance of the smoke—in order to create an up-draught, and insure the charring of the wood on the outside of the heap. Small piles take six to fourteen days to carbonise, large ones one month. Rectangular heaps are sometimes used, the walls being made of stakes and rough boards.

By conversion into charcoal by burning in heaps, wood loses on an average some 25 per cent. of its bulk, and 75 to 80 per cent. of its weight. Its apparent specific gravity—*i.e.*, including pores—varies from 0·2 to 0·5, according to the wood from which it is derived. The real specific gravity is from 1·5 to 2·0. Beechwood charcoal produced by this method has the following composition:—Water, 7·0 per cent.; carbon, 86·2 per cent.; H, 2·3 per cent.; O and N, 1·5 per cent.; ash, 3·0 per cent. On keeping, the moisture may increase to about 12 per cent., which diminishes the value of the charcoal as a fuel (Vol. I., p. 56).

In general, the products of the destructive distillation, other than charcoal, escape or are burnt, but by building the meiler on a concave brick floor, a portion of the tar is caught and recovered. The difficulty of generally adopting this plan, is that the brick floor necessitates that the heap should be kept to one place and the wood brought to it. The rectangular heaps are

better adapted for the recovery of tar, as they are worked from one end to the other and the draught carries the tar continuously in the direction of the length of the heap. Lime has been proposed as a covering, for fixing the acetic acid (one of the products), and other coverings sufficiently rigid to admit of the introduction of pipes have been tried. The objections to both arrangements is that unless the cover be flexible it will not fall in as the wood shrinks.

(B) **CHARRING IN KILNS.**—The kilns, which are chiefly used in America, are rectangular brick structures with an arched roof, some 40 to 50 feet long and 12 to 18 feet wide, and about 12 to 18 feet to the spring of the roof, holding 100 to 180 tons, or cylindrical structures 28 feet in diameter, 12 feet high, and covered with a dome. In either case vent-holes are left in the walls, and are opened and closed according to the supply of air required. The charring takes 6 to 10 days, and 4 to 6 days are needed for cooling. The products are not recovered in these kilns; those forms designed for the recovery of products are of beehive shape, and the air has access to the charge through a grate. The entry of air is stopped as soon as the walls are hot enough to complete the charring. The kiln is filled partly through the door and partly through a hole in the top which is closed before ignition. A pipe in the upper part of the kilns leads the products through a condenser.

(C) **CHARRING IN RETORTS.**—Many forms of retorts are used; they are generally made of boiler plate and set horizontally, although cast iron is also used as a material and the setting is vertical in many cases. The size varies considerably, but 3 feet diameter by 8 feet long is not unusual. The charge for a retort of this size is about 6 cwts. The retorts are heated by the flame of the gas evolved from the distillation, supplemented by a little wood or charcoal.

The general arrangement for the distillation of wood in retorts is shown in Fig. 19, in which A is the retort, set in the furnace, B, in which the fire from the grate, C, circulates round the retort, the furnace gases finally passing away by the flue, D. The products of distillation pass through the condensing pipe, E, set in the water jacket, F. The liquid products flow through the small pipe, G, into the trough, H. The uncondensed gas passes through the pipe, K, into the main, L, which is common to several retorts, and whence the gas finally passes through the pipe, M, into the grate, C. The door, N, of the retort is removed when the distillation is complete, and the contents of the retort are pulled out bodily by a windlass attached to the bar and frame, O.

The quantity of charcoal obtained by distillation in retorts is about 27 per cent. of the weight of the wood, but of this some 5 per cent. is necessary for heating the retort, so that the net

result is no better than when burning in heaps is used. The value of the distillate constitutes the chief advantage of distillation in retorts.

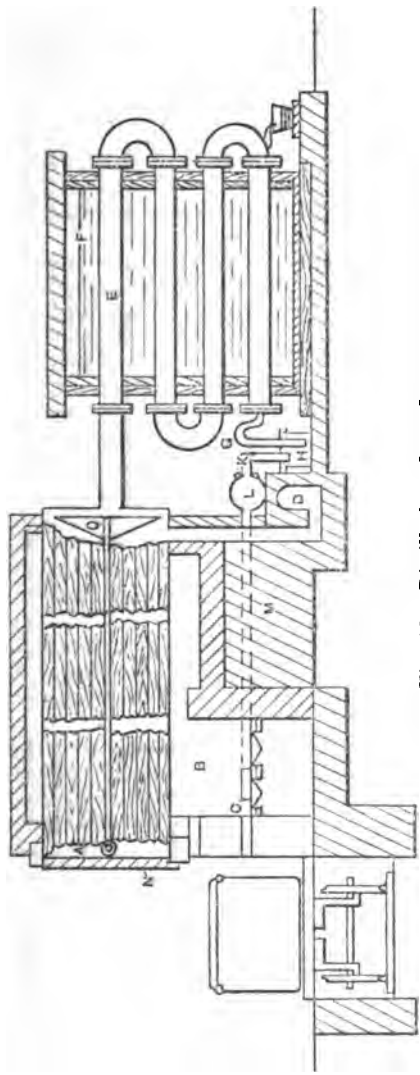


Fig. 19.—Distillation of wood.

A, Retort; B, furnace; C, grate; D, flue; E, condensing pipe; F, water jacket; G, small pipe; H, trough; K, pipe; L, main; M, pipe leading to grate; N, door of retort; O, bar and frame.

PRODUCTS.—These are charcoal, tar, crude acetic acid, spirit and gas.

(*a*) **Charcoal.**—The average yield from the wood of two typical trees is :—*

	Crude proligneous acid (watery distillate).	Acetic acid (glacial) in watery distillate.	Tar.	Charcoal.	Gas.
Oak, . . .	47·6	5·4	6·4	24·9	22·1
Scotch fir, . .	45·0	2·7	10·0	28·0	27·0

In each case the watery distillate contains about 1 per cent. of wood spirit, reckoned on the wood.

With regard to the quality of the charcoal produced by these several methods, it depends on (1) the nature of the wood, and (2) the temperature of distillation. The hard close-grained woods, such as oak and beech, give a hard dense charcoal, while woods of lighter and looser texture, particularly woods of conifers, give a correspondingly soft charcoal. The higher the temperature of distillation the blacker the charcoal, and the more nearly it approaches pure carbon (Vol. I., p. 56). Charcoal is also made at very low temperatures (360° to 520° C. = 680° to 968° F.) for gunpowder making, superheated steam being sometimes used for charring. The qualities prepared at the lowest temperatures are brown in colour, and are known as red charcoal (*charbon roux*). It is less porous and hygroscopic, and more inflammable than black charcoal, and has, when freshly made, the average composition, 74 per cent. C., 24·5 per cent. O and H, and 1·5 per cent. ash. After a time it will be found to have taken up as much as 10 per cent. of water. For further information concerning low temperature charcoal see *Explosives*, Vol. II., Chapter XVII.

Besides its use as a fuel, which has already been dealt with in Vol. I., p. 56, charcoal is applied as a deodoriser on account of its property of absorbing, and to some extent oxidising, objectionable gases. This oxidation is effected by the atmospheric oxygen which the charcoal has absorbed during cooling and storage. 1 vol. of charcoal can occlude 9·25 vols. of O, and similarly large quantities of other gases. High temperature charcoal takes up less gas than a low temperature product. The application for filtering water depends upon the same principles. Being a non-conductor, charcoal is used as a packing to hinder the transmission of heat.

(*b*) **Wood Tar.**—The yield of tar varies from 7 to 10 per cent. of the wood, rising to 14 per cent. in the case of pine wood. Wood tar is characterised by the large proportion of oxygenated bodies it contains. Tar condensed from the distillate from wood

* Fawsitt, *Journ. Soc. Chem. Ind.*, 1885, p. 319.

distilled in closed retorts varies according to the nature of the wood, that from the conifers being rich in terpenes, due to the decomposition of the resinous constituents of the wood; that from other woods, such as beech, contains hydrocarbons of the paraffin and benzene series, together with various phenols and their derivatives.

Stockholm tar is that which is most commonly used as a preservative for wood, and is produced from coniferous woods by a process of distillation in which it is the most valuable product; the process consists in filling the wood into large holes, shaped like inverted cones, in the ground. The wood is ignited at the top, and allowed to burn slowly, access of air being hindered by partially covering the pile with earth; the tar collects in a trench at the bottom.

Russian tar is characterised by being specially rich in pyrocatechol (see *Leather*, Vol. II., Chap. XVI.).

In America, crude wood-tar creosote oil from coniferous wood is substituted for coal-tar creosote in creosoting sleepers and piles (Vol. I., p. 47).

Purified Wood-tar creosote is obtained by separating the tar into two fractions by distillation, and washing the heavier fraction with caustic soda, whereby creosote is dissolved. The alkaline solution is boiled in air to oxidise impurities, and precipitated with sulphuric acid; these two processes are repeated, and the product distilled; the fraction from 200° to 220° C. = 392° to 428° F. constitutes commercial wood-tar creosote, which contains 50 to 60 per cent. of guaiacol, $C_6H_4(OH)(OCH_3)$, and creosol, $C_6H_3CH_3(OH)(OCH_3)$, together with small quantities of many other phenolic derivatives. It is a powerful antiseptic, and much used in medicine.

(*c*) **Wood Spirit.**—The distillate from wood consists of a mixture of tar and watery liquid, the latter containing acetic acid and wood naphtha or wood spirit. The tar is separated by subsidence and used for the purposes already mentioned, and the watery liquid is drawn off from the top, and worked up for acetic acid, acetone and methyl alcohol. The method of working up varies according to what grade of acetate of lime is to be prepared. If **brown acetate of lime** (*v.i.*) be required, the crude watery distillate (pyroligneous acid) is neutralised at once with lime and distilled in an iron still until the spirit has come over, and the distillate (about 20 per cent. of the whole) is too weak in inflammable constituents to flash when thrown on to glowing cinders (a preferable test is the specific gravity of the liquid). The acetate of lime remains in the retort. If **grey acetate of lime** be needed, the pyroligneous acid is distilled, to remove tarry matter, in copper retorts—iron being attacked by the acid—heated by coils conveying superheated steam, and the distillate either collected in two fractions, the first being the spirit, and

the second the acetic acid, or neutralised with lime and redistilled until the spirit has come over. Crude wood spirit is a complex liquid containing methyl alcohol, acetone, methyl acetate, aldehyde, allyl alcohol, and dimethyl acetal, with small quantities of the three methylamines, ammonium acetate, oils of the aromatic series, and tarry matter. It is distilled with excess of lime, which retains water, hydrolyses methyl acetate into methyl alcohol and calcium acetate, and to some extent decomposes the amines. The distillate consists of methyl alcohol and acetone, together with ammonia and small quantities of amines; for the complete retention of these and of the ammonia, subsequent distillation over a small quantity of sulphuric acid may be adopted. The most important point in the purification is the hydrolysis of the methyl acetate, as the presence of this body makes it difficult to get the specific gravity of the finished product down to the limit set by the Excise (see *Brewing* and *Distilling*, Vol. II., Chap. IX.). The oils must be eliminated as completely as possible, as they cause the spirit not to be "miscible"—*i.e.*, capable of mixing with water without producing a turbidity. This separation is sometimes effected by diluting with water until precipitation of the oils occurs, shaking with melted paraffin wax, filtering, and distilling.

The finished wood naphtha (wood spirit) is nearly colourless; its specific gravity is 0·827, corresponding with a strength of 61° over proof. It contains 80 per cent. of methyl alcohol, 6 per cent. of acetone, and 12 per cent. of water, besides traces of empyreumatic products that give it a disagreeable taste and smell, and fit it for denaturing alcohol (see *Brewing* and *Distilling*, Vol. II., Chap. IX.), which is its main use. The rest goes for aniline colour making (*q.v.*), as a solvent in varnish making, and for burning in lamps.

Acetone, $(CH_3)_2CO$, which is also an article of commerce, can be made by distilling the wood spirit over calcium chloride, which retains the methyl alcohol, but it is generally prepared (for making chloroform) by the distillation of acetate of lime. Pure **methyl alcohol**, CH_3OH, may be recovered from its calcium chloride compound ($CaCl_2 . 4CH_3OH$) by distillation with water and subsequent dehydration with lime. The method generally used, however, consists in passing dry chlorine through boiling wood spirit, whereby the acetone is converted into chlorinated products of high boiling point, and fractionally distilling the methyl alcohol from these. The pure alcohol boils, according to the latest authorities, at 65° C. = 149° F.; its specific gravity, when anhydrous and also when diluted with water, is nearly identical with the value for ethyl alcohol of the same strength.

(*d*) **Acetic Acid and Acetates.**—The yield of acetic acid varies greatly; the following are some figures illustrating this:—

	Glacial Acetic Acid.
Lime, . . .	10·24 per cent., reckoned on the wood.
Aspen, . . .	8·06 ,, ,, ,,
Pine, . . .	5·65 ,, ,, ,,
Birch bark, . .	2·20 ,, ,, ,,

For further information concerning acetic acid see *Vinegar*, Vol. II., Chap. IX.

The chief commercial acetates include brown and grey acetate of lime, brown sugar of lead, and acetates of iron (*pyrolignite of iron*, *iron liquor* or *black liquor*). For the **brown acetate of lime** the crude pyroligneous acid is neutralised with powdered chalk or lime, and sometimes distilled to recover the wood spirit (*v.s.*), and sometimes evaporated directly to dryness, preferably by steam heat, the salt fished out as it separates and dried in kilns at a temperature of about 125° C. = 257° F. Its colour is due to tarry matter. It contains 70 to 75 per cent. of real acetate of lime, $(C_2H_3O_2)_2Ca$, the balance being water, tarry matter, and excess of lime as carbonate. The **grey acetate** is similarly prepared from the pyroligneous acid that has been once distilled to free it from tarry matter. Acetate of lime is used for the manufacture of acetic acid (by distillation with sulphuric acid), and other acetates, and for calico-printing.

Brown sugar of lead (crude lead acetate) is the product of the neutralisation of once-distilled pyroligneous acid with litharge. The mixture is boiled and well stirred, skimmed, and crystallised. It is used in the preparation of alum mordants (see *Dyeing*, Vol. II., Chap. XIII.).

Pyrolignite of iron is a solution of crude ferroso-ferric acetate, containing a little pyrocatechol, which gives it its black colour. It is made by dissolving scrap iron at a temperature of 65° C. = 149° F. in crude pyroligneous acid of specific gravity 1·04. The liquor is evaporated to a specific gravity of 1·13, when it contains about 10 per cent. of iron. It is used in *Dyeing and Calico-Printing*, Vol. II., Chap. XIII.

(*e*) **Gas.**—Crude wood gas contains about 53 per cent. of CO_2; when freed from CO_2, the gas contains CO, 82 per cent.; CH_4, 14 per cent.; C_2H_4, 0·75 per cent., and the balance nitrogen. Gas of this composition is of little illuminating value, and only serves for heating the retorts. That produced by the distillation of resinous wood—*e.g.*, pine—may, on the other hand, be rich in illuminants, but is of no value till freed from CO_2 by lime purifiers (see *Coal Gas*, Vol. II., p. 65).

The relative quantities of the products of the destructive distillation of wood at varying temperatures have been determined by laboratory experiments made by Ramsay and Chorley* on wood, on pure jute fibre, and on cotton wool (cellulose). They have incidentally noticed that when the wood or jute fibre is

* *Journ. Soc. Chem. Ind.*, 1892, pp. 395 and 872.

heated in a flask, surrounded by an air bath, a sudden rise of temperature in the interior of the flask to a point some 50° C. above that of the air bath, takes place at a temperature of about 300° C. = 572° F. They consider this to be evidence that the destructive distillation of wood is accompanied by an exothermic reaction. They have observed that at this temperature the products, which are similar in the main to those obtained on the large scale, are formed in largest quantity. At 500° C. = 932° F. the percentage of charcoal is considerably lower than at 360° C. = 680° F., and the percentage of gas a good deal higher. The yield of acetic acid is little influenced. Different woods gave a fairly constant yield of acetic acid but no experiments with resinous woods were made.

III. DESTRUCTIVE DISTILLATION OF SHALE.

Shale is a carbonaceous mineral which appears to have been formed from the remains of marine animals and plants, mixed with argillaceous mud, consolidated into a slaty mass. The Scottish shales, which may be taken as typical of their class, are below the coal measures, and accompany strata of marl, limestone and sandstone. The nature of the carbonaceous matter in the shale is unknown, but, inasmuch as none of the substances obtained by the destructive distillation of the shale can be directly extracted from it by solvents, it may be certainly stated that such substances do not pre-exist in the shale.

The average composition of Broxburn shale is C, 20 per cent.; H, 3 per cent.; O, 0·5 per cent.; N, 0·7 per cent.; S, 1·5 per cent.; ash, 69·8 per cent. The ash consists of silicates approximating in composition to a ferruginous impure clay, and is often tolerably fusible. The main difference between shale and cannel coal consists in the percentage of ash, rich shales approximating to cannel in their composition; this is well illustrated by the New South Wales "kerosene shale," which contains only 8 per cent. of ash, and a splinter of which will burn like cannel. The winning of the shale is conducted similarly to the winning of coal; at Broxburn it crops out at the surface, but nowadays has to be mined. The process of distillation differs from those previously considered in that it is conducted at a much lower temperature, and is, in most cases, aided by the injection of superheated steam. It must be noted that the object of this distillation is the production of paraffinoid hydrocarbons, for the obtainment of which the shale is particularly adapted, doubtless both on account of the specific nature of the bituminous matter present, and because of its being spread over a larger surface of inert matter (the ash) tending to prevent condensation into benzene hydrocarbons; should the temperature be allowed to

rise, such condensation would tend to occur even as it does in the high temperature distillation of oils conducted for the manufacture of oil gas (Vol. II., p. 74).

The nature of the products may be gathered from the average yield at Broxburn :—

	Per cent.	
Volatile matters.		
Crude oil or tar,	12	
Ammoniacal liquor,	8	
Gas,	4	
Total,	—	24
Non-volatile (spent shale).		
Combustible,	9	
Ash,	67	
Total,	—	76
		100

The apparent discrepancy between these figures and those given above for the ultimate composition of the shale is to be accounted for by the fact that the injected steam is condensed with the ammoniacal liquor, and increases the total amount of products obtained.

In modern practice two types of retorts are used for the distillation, the improvements on the older forms consisting in affording facilities for consuming the "fixed carbon" of the spent shale (corresponding with coke from coal) as fuel for heating the retorts. Both types are on this account set vertically. In the older of the two, of which the Henderson retort (Fig. 20) may be taken as an example, the retorts are closed vessels heated by a separate furnace into which the spent shale can be dropped by withdrawing the bottom plate of the retort when the charge is worked out. In the more modern type, such as the Young and Beilby (Fig. 21), the lower part of the retort serves as a combustion chamber for heating the material in the upper, so that no hard and fast distinction can be drawn between the retort and its furnace. The details of construction will be readily comprehended from the accompanying figures.

Fig. 20 represents the Henderson plant. Four cast-iron retorts, of which a pair is shown in the figure, A, A, 15 feet long and of elliptical section ($2\frac{1}{2}$ feet by 1 foot), with walls $1\frac{1}{4}$ inches thick, are set in a firebrick casing over a furnace, B, divided by a vertical partition. They are charged from the top, and one of the set is discharged into the furnace every four hours by drawing back the bottom plate, C. The products of distillation are led off at the lower part of the retort by a pipe, D. The retorts are protected from direct contact with the flame by the firebrick arch, E, the furnace gases passing up the flue, F, and finally escaping by the pipe, G, which is at the bottom of the furnace, and of small sectional area in order that the draught may be

sufficiently gentle for the combustion of the spent shale. The non-condensable gases from the distillation (*v.i.*) are also turned into the furnace through the pipe, H. Superheated steam is admitted to the retorts by the pipe, K, to aid the process of distillation.

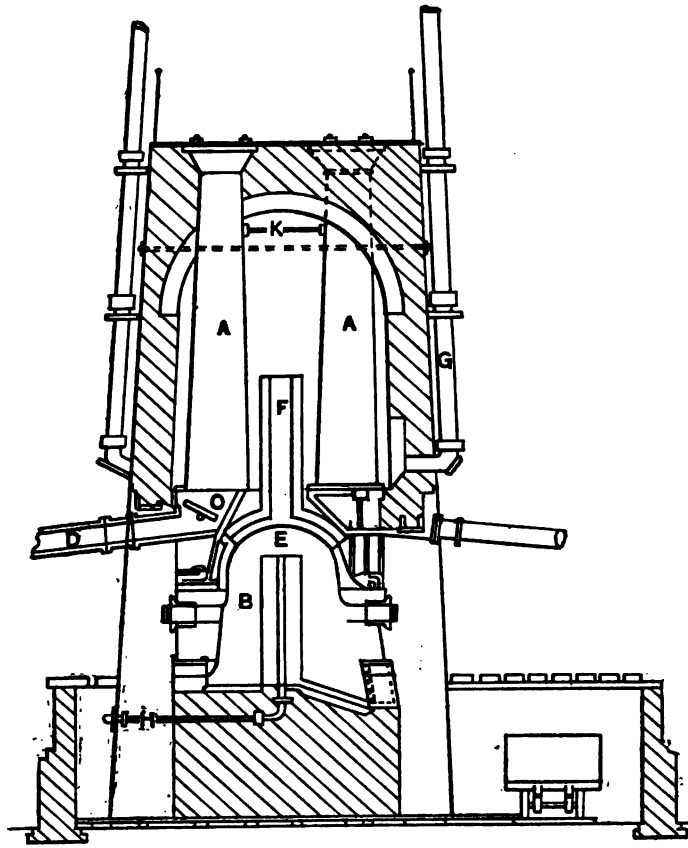


Fig. 20.—Henderson shale retort.

A, A, Retorts; B, furnace; C, bottom plate; D, products pipe; E, firebrick arch; F, flue; G, flue gas pipe.

Fig. 21 shows the Young and Beilby retort, which, like the Henderson, is set in groups of four, and consists of an upper part, A, of cast iron, some 9 feet long, circular or elliptical in section, placed above a firebrick portion, B, about 8 feet long, of oblong section—1 foot 11 inches by 10 inches at the upper end, and 2 feet 5 inches by 12 inches at its widest point. The ends

are curved outwards to admit of the discharge of the consumed spent shale at the side. The destructive distillation of the shale takes place in the upper cast iron part of the retort, and by the time the material reaches the lower firebrick portion it contains nothing but "fixed carbon," which is there consumed by a current of air injected at C. Steam is also blown in at these

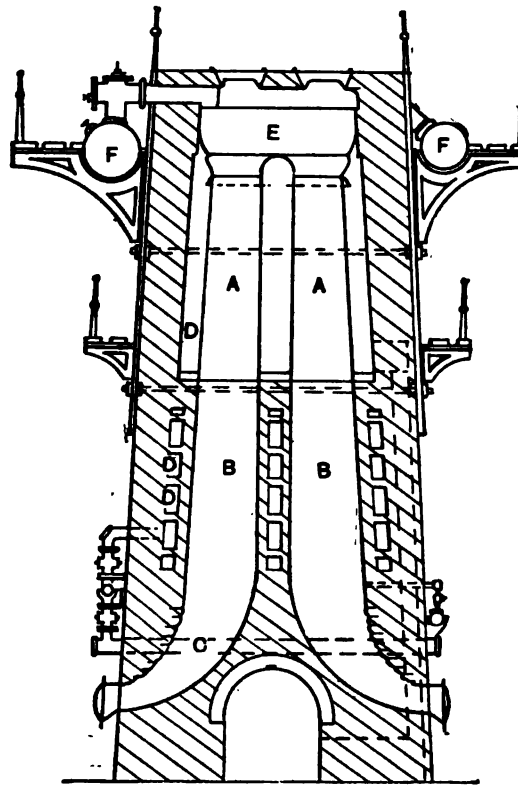


Fig. 21.—Young and Beilby's shale retort.

A, Upper part (iron); B, lower part (firebrick); C, place where air current is injected; D, flues; E, hopper; F, mains.

points to aid in the production of ammonia (*v.i.*), and, in some forms of plant, supplementary external heating is adopted by burning producer gas in flues (D) surrounding the retorts.

The admission of air without steam into the retort would be more effective as far as producing heat for the oil distillation, which takes place in the upper part of the retort, is concerned,

but the use of steam is necessary to favour the production of ammonia. A multiple hopper, E, serves for feeding the retorts, which are worked continuously; the products of the distillation pass through the green shale in the hopper, serving to raise its temperature, and into the mains, F.

It will be noted that modern practice in shale distillation is tending to the use of retorts analogous to the common gas producer worked for the production of oil and ammonia as the main products, and, therefore, driven at as low a temperature as possible, so as to confine the combustion to its lower part, and carry on distillation in its upper part.

The general system of plant for the recovery of the products of distillation of shale resembles that used in the manufacture of coal gas, particular care being taken to recover the oil (equivalent to gas tar), which is the main product of the process, rather than the gas, which is of subsidiary importance being merely burned under the retorts.

PRODUCTS.—The nature of these has been already indicated (*v.s.*); the oil being the most important may be considered first:—

(*a*) **Crude Oil or Tar.**—This is collected from the condensers (which are air condensers; see p. 62), and amounts to some 30 gallons per ton in the case of the Broxburn shale. It is of greenish colour, and semi-solid from the presence of paraffin wax.

Its quality depends on the class of retort used; that from the old vertical retorts and the Henderson has a specific gravity of 0·89, and is more tarry—that is, contains a larger proportion of overheated and coked products; this is shown by its leaving 5·10 per cent. of coke on distillation, which is, however, valuable as being free from ash and sulphur. The tar from the newer forms of retort (Young and Beilby) has a specific gravity of 0·87, and is so free from tarry matter that it may be worked as once-run oil (*v.i.*). It is separated from ammoniacal liquor in settling tanks, and is pumped into cast-iron stills holding up to 2,000 gallons, and resembling tar stills (p. 77). From these it is distilled as far as possible, when it is known as once-run oil; but in modern practice the crude tar is distilled continuously in sets of three oblong stills with arched roofs and concave bottoms. In the first still the distillation is carried to the point when the fraction known as "green naphtha" (specific gravity 0·753) has come over, the residual oil being passed into the second still where the distillation is carried to the point when heavier oils, of specific gravity about 0·835, come over; after this the remaining oil goes into the third or coking still where the distillation is carried to the coking point, the distillate ranging in specific gravity from 0·860 to 0·965. By this method the first two stills do not have to be stopped for clearing, as all the coke is deposited in still

No. 3, which is used in duplicate so that one may be running while the other is being cleared. The fraction from the first still (green naphtha, specific gravity 0·753) corresponds with the first fraction (naphtha) from the redistillation of the once-run oil when the old intermittent process, similar to tar-distilling (p. 77), is used.

This fraction is purified by successive treatment with caustic soda and sulphuric acid, and is marketed as solvent naphtha (benzine or benzolene), or is used on the works for purifying paraffin wax. The description of the further operations applies to the continuous process, the older intermittent process being similar in principle. The heavier fractions from stills 2 and 3 (green oil) are mixed and redistilled to obtain two fractions, light and heavy oils. The light oil is obtained by distilling until a specific gravity of about 0·850 is attained; this oil yields the illuminating oil, of which there are several grades, distinguished by their specific gravity, and for the obtainment of these the light oil is redistilled. The bulk of Scotch illuminating paraffin oil ranges in specific gravity from 0·800 to 0·820, and is similar to American kerosene as an illuminant (*q.v.*), but has usually a higher specific gravity and flashing point (see *Petroleum*, Vol. II., Chap. V.). Chemically, the two differ on account of the larger proportion of olefines in shale oil, as indeed is indicated by its odour. The heavy oil contains the paraffin wax, and is cooled until the "crude scale" separates; this is removed by a filter press, and the still liquid portion, "blue oil," cooled again for a further yield. The blue oil is then redistilled, and the fraction treated with caustic soda and sulphuric acid to obtain the different grades of lubricating oil, ranging in specific gravity from 0·865 to 0·900. The treatment of the blue oil (this applies also to the lighter illuminating oils) consists in agitating it in wrought-iron tanks first with the strongest vitriol (the concentrated acid not acting on the iron) for a few hours at a temperature as low as practicable, to avoid acting on the olefines, and allowing it to settle; the acid combines with basic impurities, and the quantity must be regulated to remove these without attacking the olefines, which are more easily attacked than are hydrocarbons of the paraffin series. The settled matter is known as "black tar" or "vitriol tar," and is run off from below and used again, should the system of distillation adopted involve the production of a cruder oil at an earlier stage; in the contrary case it is washed with hot water to remove the sulphuric acid, and injected, together with steam, into the furnaces, serving as a fuel. Another plan, suggested by Rave, consists in treating the tar with iron borings, and obtaining as a final product a bituminous substance useful for coating battery tanks and for making varnish. The acid-washed oil is treated with caustic soda (specific gravity 1·3), which removes acid impurities. It is black when the treatment has been properly

conducted, but otherwise may be a white gelatinous mass (see *Petroleum, Solidification of*, Vol. I., p. 58). As the impurities removed by soda are phenolic bodies, they may be recovered by precipitating the soda solution with CO_2, the resulting sodium carbonate being causticised and used again. The finished lubricating oils appear to owe their properties to the presence of iso-paraffins, the normal compounds being poor lubricants.

Paraffin scale or crude **paraffin wax** is the most valuable and characteristic constituent of shale oil. The solid portion of the heavy oil, separated by filtration, is submitted to one of three processes. One of these consists in heating it with vitriol at a temperature not exceeding 60° C. = 140° F., then with caustic soda, and finally thoroughly washing with water, the object of the process being to attack the oily products and leave the crystalline wax. Another, which is more often employed, is that in which the scale is crystallised several times from shale naphtha (*v.s.*), the solution being filtered through animal charcoal or similar decolorising agent, and the crystalline mass pressed to get rid of the last of the solvent. The rationale of this process rests on the fact that the paraffins of low melting point are more soluble than those of high melting point. The third is a process of liquation, or "sweating," and is effected by casting the crude scale into thin cakes and compressing it between mats of cocoa-nut fibre in hot presses, the more fusible substances being thereby expressed. The chief use of paraffin wax is in candle manufacture (*q.v.*), but it is also used as a waterproofing material for matches, paper, &c., and as an electrical insulator. When put on the market it should be white and well crystallised; its price is greater the higher the melting point, which ranges from 45° to 60° C. = 113° to 140° F. The average yield from crude shale oil is as follows:—

Naphtha,	5	per cent.
Illuminating oils,	37	,,
Lubricating oils,	17	,,
Paraffin wax,	13	,,
Loss,	28	,,
	100	,,

(*b*) **Ammoniacal Liquor.**—This mainly differs from gas liquor in containing a smaller quantity of sulphur compounds. It amounts on the average to 65 gallons per ton of shale, which quantity may be increased to 120 gallons per ton when much steam is used in the distillation. The amount of ammonium sulphate obtained from the liquor varies with the type of retort used, the Henderson yielding from 16 to 20 lbs. per ton of shale, and the Young and Beilby twice as much, the quantity being further increased by the ammonia recovered from the producer

gas used as an auxiliary source of heat. The distribution of the nitrogen of the shale is about 20 per cent. as ammonia, 50 per cent. in the spent shale, and the remainder in the tar and gas. In processes like that of Young and Beilby, where the spent shale is treated with steam, a portion of the nitrogen is removed and increases the yield of ammonia. The bulk of the ammonia in the liquor is as carbonate; the liquor is distilled in a column still (see *Brewing* and *Distilling*, Vol. II., Chap. IX.), and the ammonia passed into sulphuric acid, which may be that which has been recovered from the acid tar. The general process of making ammonium sulphate is similar to that adopted for gas liquor (p. 76).

(*c*) **Gas.**—The gas evolved in distillation contains hydrocarbons of the paraffin and olefine series. About 2,000 cubic feet per ton of shale are obtained at Broxburn. By passing the gas through scrubbers, kept moist with heavy oil, nearly 3 gallons of gasolene (a mixture of light hydrocarbons) can be obtained per ton of shale. The gasolene is recovered by heating the oil used to collect it, and is employed for carburetting air for illuminating purposes. The rest of the gas is used for firing the retorts and lighting the works.

IV. DESTRUCTIVE DISTILLATION OF BONES.

The main object of bone distillation is the production of animal charcoal (bone-black), valuable bye-products being oils and ammonia. It will be seen below that the organic portion of the bone is comparatively small in amount, so that the coke is rich in mineral matter, containing only about 10 per cent. of carbon. Bone appears to be a cartilaginous tissue which has become impregnated with calcium phosphate and carbonate, removable by treatment with dilute hydrochloric acid, the original skeletal mass of organic matter being left. The composition of bone varies with the kind of animal—and its condition and age—from which the bone has been obtained. The following is a representative analysis of dry bone:—

	Per cent.	
Fat, ...	6	
Nitrogenous matter (Osseine),	28	
Mineral matter, . .	66	consisting of calcium phosphate, 56 per cent.; calcium carbonate, 8 per cent.; magnesium phoshate, 1 per cent.; calcium fluoride, 1 per cent.
	100	

The water varies, about 20 to 25 per cent. being an average amount. The fat is extracted either by melting it by heating with steam, with subsequent addition of cold water (which removes 4 to 5 per cent. of fat), or by dissolving it in volatile

solvents (which extract 6 to 8 per cent. of fat), such as light petroleum, carbon bisulphide, &c.; it is used for soap making (*q.v.*). The fat-free bone is either used as manure (p. 111) or boiled for glue, which process converts the osseine into gelatine and extracts it, the boiled bones being used as manure. The fat-free bones from which the osseine has not been extracted are those used for bone-black manufacture, for which purpose they are carbonised, according to Continental practice, in covered iron or fireclay pots, the products being allowed to escape, partly on account of the difficulty of separating them from the furnace gases, and partly because the most volatile constituent (ammonia) is decomposed by the high temperature employed. In this country, the distillation is usually carried out in iron or fireclay retorts similar in most respects to coal-gas retorts, the charge varying from 2½ to 3½ cwts.; the products are collected in condensers similar to those used in gas works, and may be considered under the following heads:—

(*a*) **Charcoal.**—This contains a very small quantity of carbon spread over a large surface of mineral matter. The following analysis is due to Newlands Bros.:—

	Per cent.	
"Carbon,"	10·51	containing 10 per cent. of its weight of nitrogen.
Calcium and magnesium phosphates, calcium fluoride, &c.,	80·21	
Calcium carbonate, . .	8·30	
Calcium sulphate, . . .	0·17	
Ferric oxide, ...	0·12	
Silica, ...	0·34	
Alkali salts, ...	0·35	
	100·00	

Moisture originally present, 8·00 per cent. The yield of "char" should be about 65 per cent. of the original bones. It is cooled in covered vessels, and passed through a magnetic separator, which removes metallic iron accidentally present, this being objectionable to the sugar refiner. The higher temperature in the pot method of carbonisation causes the charcoal to be of better quality than that produced in retorts. Besides its application in sugar refining, the charcoal is used for filtering and decolorising water, oil, paraffin wax and glycerine. The pigment called "ivory black" is generally finely-divided bone black. When once exhausted in these various uses, bone black can be revivified by burning, and this process can be repeated several times (see *Sugar*, Vol. II., Chap. VIII.), but the char eventually becomes spent, when it is sold to the manure maker.

(*b*) **Oil.**—*Bone oil* (*Dippel's oil, animal oil*) is derived from the osseine and any residual fat there may be in the bone.

The former is highly nitrogenous, as shown by the following figures:—

C,	50·4	per cent.
H,	6·5	,,
N,	16·9	,,
O,	26·0	,,
S,	0·2	,,
	100·00	,,

Bone oil is, therefore, richer in nitrogenous derivatives than is the tar from coal, wood or shale. It is a dark-brown liquid (specific gravity 0·914 to 0·970) of offensive smell, and amounts to 3 to 5 per cent. of the bones carbonised; it contains fatty nitriles, pyrrol and its methyl derivatives, hydrocarbons of the series C_nH_{2n-4}, various compound ammonias and pyridine bases. It is redistilled, when much ammonia in the form of carbonate and cyanide comes off, together with the oil, and a black resinous tar remains and is used for making Brunswick black. The oil is now used, on the Continent, for denaturing spirit, and a small quantity is worked up for the pyrrol, C_4H_4NH, it contains, which is converted into tetraiodopyrrol, C_4I_4NH, employed as an antiseptic in place of iodoform. The richness of the oil in pyridine, C_5H_5N, and similar bodies, to which the vegetable alkaloids are closely allied, opens up the prospect of synthesising these latter from bone oil. Coniine (the alkaloid of hemlock) has been already prepared from picoline (methyl pyridine), obtained from bone oil. At present, on account of the fœtid odour of the oil, it is mostly burnt under the retorts.

(*c*) **Ammonia.**—At one time the distillation of bones was the chief source of ammonia, but its importance has decreased since the birth of coal-gas manufacture. The proportion of ammonia, reckoned as ammonium sulphate, is about 6 to 7 per cent. of the weight of the bones distilled. The resulting ammonium sulphate is usually highly coloured, from the presence of pyrrol red.

(*d*) **Gas.**—A good deal of gas of high illuminating power is given off during distillation, but it contains too much sulphur to be readily purified, and is, therefore, burnt at the works either for lighting or for heating retorts and boilers.

CHAPTER IV.

ARTIFICIAL MANURE MANUFACTURE.

A MANURE is a substance designed to supply one or more of the essential constituents of plant food, and, where necessary, to improve the physical condition of the soil to which it is applied. The essential constituents of plant food must contain the elements C, H, O, N, P, S, K, Ca, Mg, Fe, and probably Si, Cl, and Na. Of these, C, H, O, and some of the N are derived from air and rain; most of the nitrogen and the remaining elements being obtained from the soil. Almost every soil will contain enough Ca, Mg, S, Fe, Si, Cl, and Na for the growth of a full crop, but N, P, and K are often present in but small quantity, and become exhausted by the removal of farm produce.

A **general manure** is usually understood to be one which can supply these three constituents, but inasmuch as some crops either contain an excess of one or other of these, or are better able to obtain some one or other of them from the soil, than are other crops, it is frequently economical to apply a special manure to meet the needs of such crops. For what is known as to the requirements of individual crops, a work on agricultural chemistry must be consulted. It thus happens that **special manures** are divided into phosphatic, nitrogenous, and potash manures. It is necessary, in order for a manure to be efficient, that it shall not only contain the requisite constituent or constituents of plant food, but that the nutriment shall be in an assimilable form, and it has been ascertained that in whatever condition the plant food may be actually absorbed, the absorption takes place the more rapidly the more soluble the food constituents.

(A.) **PHOSPHATIC MANURES.**—The only abundant form in which phosphorus is found, is as the various forms of calcium phosphate (phosphate of lime), and, to a smaller extent, as aluminium and iron phosphates. Of these, the calcium phosphates are better capable of supplying phosphorus to the plant than are iron and aluminium phosphates, probably because of the greater ease with which this compound is dissolved by feeble acids — *i.e.*, carbonic acid — and by saline solutions. Deposits of calcium phosphate are widely distributed. The most definite mineral containing calcium phosphate is **apatite**,

$3Ca_3(PO_4)_2 . CaCl_2$ or $3Ca_3(PO_4)_2 . CaF_2$, both varieties being known. It contains 70 to 80 per cent. of calcium phosphate. The less nearly pure apatites, known as **phosphorites**, are obtained chiefly from Estramadura (containing 50 to 70 per cent. of $Ca_3(PO_4)_2$), and from Canada (containing 70 to 80 per cent. of $Ca_3(PO_4)_2$). They are associated with quartz and calcium carbonate. Other deposits of calcium phosphate, less distinctly characterised as minerals, are found in Carolina, the West Indian Islands, France, Germany, and Belgium, and in Cambridge and Suffolk. The form known as **coprolites**, supposed to be fossilised animal excreta, occurs in England and France, the Cambridge deposits being the best (55 to 60 per cent. $Ca_3(PO_4)_2$). The South Carolina phosphate is known as "**land phosphate**" and "**river phosphate**," the latter being obtained by dredging. West Indian phosphates, or Caribbean phosphates, are not all available for superphosphate manufacture (*v.i.*), as some of them contain much iron and aluminium, the variety known as Redonda phosphate being mainly aluminium phosphate. Their use is consequently limited. Florida phosphates exist in the form of pebbles, and massive as rock. They vary considerably in richness—*e.g.*, 60 to 70 per cent. $Ca_3(PO_4)_2$ for pebbles, and 75 to 80 per cent. for rock.

These phosphates, even when very finely ground, are but slowly assimilated by plants, and are, therefore, almost exclusively used for making **superphosphate**, the process consisting in treating them with sulphuric acid in order to realise the equation—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + \underset{\text{Superphosphate}}{CaH_4(PO_4)_2},$$

as nearly as is practicable, $CaH_4(PO_4)_2$ being soluble in water. Calcium carbonate, a common impurity in phosphates, consumes sulphuric acid in this treatment. Other objectionable impurities in phosphates are the ferric oxide and alumina, because both oxides form insoluble phosphates, so that the proportion of **soluble phosphate** in the prepared superphosphate is diminished by their presence. Various plans have been proposed for removing calcium carbonate—*e.g.*, treatment with an aqueous solution of CO_2 or SO_2, in which calcium carbonate is soluble; or by causticising the lime by heat, and acting upon it with an ammonium salt—*e.g.*, the chloride—the ammonia being recovered. Redonda phosphate (essentially $AlPO_4$) has been converted into an available form by treatment with sulphuric acid, yielding aluminium sulphate and phosphoric acid, or by heating with sodium chloride and superheated steam, whereby a portion of the phosphoric acid is converted into sodium phosphate.

The variation in the composition of commercial phosphates may be gathered from the following analyses (*Warington*):—

	Canadian (Apatitic).	S. Carolina (River Phosphate).	Coprolite (Cambridge).
Water, .	0·4	2·3	4·0
$Ca_3(PO_4)_2$, .	86·9	56·3	58·1
Cl and F, .	3·2	3·4	...
SiO_2, . .	1·0	14·0	8·2
CaO, . .	7·6	10·5	11·9
MgO, . .	...	0·6	1·0
Fe_2O_3 + FeO,	...	2·2	2·2
Al_2O_3, . .	...	1·3	2·0
SO_3, . .	...	1·0	0·9
CO_2, . .	...	4·6	6·8

Small quantities of minor impurities are also generally present. "**Superphosphate**" is a mixture of calcium sulphate as gypsum with the acid phosphate of lime, $CaH_4(PO_4)_2$, which is the essential manurial constituent. The crude calcium phosphate to be converted into superphosphate should be, as stated above, as free as possible from iron and aluminium compounds (not more than 3 per cent. of Fe_2O_3 + Al_2O_3) and from calcium carbonate. The material is ground very finely—*e.g.*, to pass a sieve having 80 meshes per linear inch—and is charged intermittently in 4 to 5 cwt. lots into a mixer consisting of a lead-lined wooden tank, provided with an agitator, where it is mixed with chamber acid (vitriol of specific gravity 1·53 to 1·61), run in as required from an adjacent tank. The quantity of acid needed varies with the composition of the phosphate, 13 to 18 cwts. per ton of phosphate being the usual limits. The mixer is built above a brick chamber known as the "pit" or "den," and into this the semi-fluid mass, after it has been agitated for a few minutes, is discharged through a shoot. The temperature of the mass in the pit rapidly rises to 110° C. = 230° F. Much gas is evolved (CO_2, HCl, and HF), and solidification sets in. The gases are drawn off through flues, and pass through a scrubber, necessary on account of the objectionable character of HCl, and still more of HF. When the pit is nearly full, one of the sides, which is of wood and removable, is taken down and the product dug out and passed through a disintegrator, whereby it is reduced to powder. When mixed manures, such as "grass manures," are being made, potash salts and nitrogenous materials are mixed during passage through the disintegrator. The proportion of sulphuric acid used in making a superphosphate is generally as great as possible without impairing the dryness of the finished manure. It is usually more than sufficient for the realisation of the equation given above. It is now supposed that the reaction which occurs takes place in two stages, the sulphuric acid first liberating an equivalent of phospheric acid, which then

reacts with the remaining $Ca_3(PO_4)_2$. The presence of calcium sulphate tends to solidify the mass by combining with 2 molecules of H_2O and setting like plaster of Paris.

The value of a superphosphate depends on its content of phosphoric acid soluble in water, which is commercially called "soluble phosphate"—*i.e.*, the amount of phosphoric acid found, on analysis, to be soluble, is calculated back to $Ca_3(PO_4)_2$. An ordinary superphosphate will contain 24 to 30 per cent. of soluble phosphate, 40 to 45 per cent. of calcium sulphate, and 2 to 3 per cent. of insoluble phosphate. Attempts have been made to produce superphosphates containing more soluble phosphoric acid than the quantity mentioned above, in order to save carriage; thus "double superphosphate" is made by extracting an ordinary superphosphate with water, removing the calcium sulphate by means of a filter press, and evaporating the liquor with untreated phosphate of a quality easily attacked by phosphoric acid. Such preparations may contain 80 to 90 per cent. of soluble phosphate.

When superphosphate is kept, a portion of the soluble phosphate becomes insoluble in water owing, it is supposed, to the interaction of calcium superphosphate, $CaH_4(PO_4)_2$, and normal calcium phosphate, $Ca_3(PO_4)_2$, thus—

$$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 4CaHPO_4.$$

A further action, which has been already mentioned, occurs between the ferric oxide and alumina contained in crude phosphate and a portion of the phosphoric acid, insoluble ferric phosphate ($FePO_4$) and aluminium phosphate ($AlPO_4$) being formed. Although such "**reverted phosphate**" is insoluble in water, it is more soluble in saline solutions—*e.g.*, ammonium citrate solution—than is the natural phosphate, $Ca_3(PO_4)_2$, and is reckoned as possessing a certain manurial value. These points have to be taken into consideration in the analytical examination of superphosphate.

Precipitated Phosphate.—When a mineral phosphate will not pay for conversion into superphosphate it may be used for the production of precipitated phosphate, which consists mainly of "dicalcium phosphate," $CaHPO_4$. The preparation is conducted by dissolving the phosphate in hydrochloric acid, sufficiently dilute to leave siliceous matter and much of the oxides of iron and aluminium undissolved. The solution is neutralised by lime or chalk, when the precipitated phosphate is thrown down. It has been proposed to utilise alkali waste (calcium sulphide) for this precipitation, the point of neutrality being discernable by the formation of FeS; the H_2S evolved is collected for use as a source of sulphur (see *Alkali*, Vol. II., p. 33). As already stated, this form of calcium phosphate is more valuable than $Ca_3(PO_4)_2$, and, being precipitated, is very finely divided; it contains up to 40 per cent. of P_2O_5, and is much used abroad.

Basic Slag.—It has been found within recent years that the phosphatic slag from the basic process of steel-making possesses considerable value as a fertiliser. The content of P_2O_5 varies from 10 to 25 per cent., and the average composition of the slag is—

	Per cent.		Per cent.
P_2O_5, . . .	17·5	Al_2O_3, . . .	2·0
CaO, . . .	49·6	MnO, . . .	4·0
MgO, . . .	4·7	S, . . .	0·5
FeO, . . .	9·8	SO_3, . . .	0·2
Fe_2O_3, . . .	4·1	SiO_2, . . .	8·0

According to Hilgenstock, the P_2O_5 exists as a calcium phosphate, of the composition indicated by the formula $4CaO.P_2O_5$.

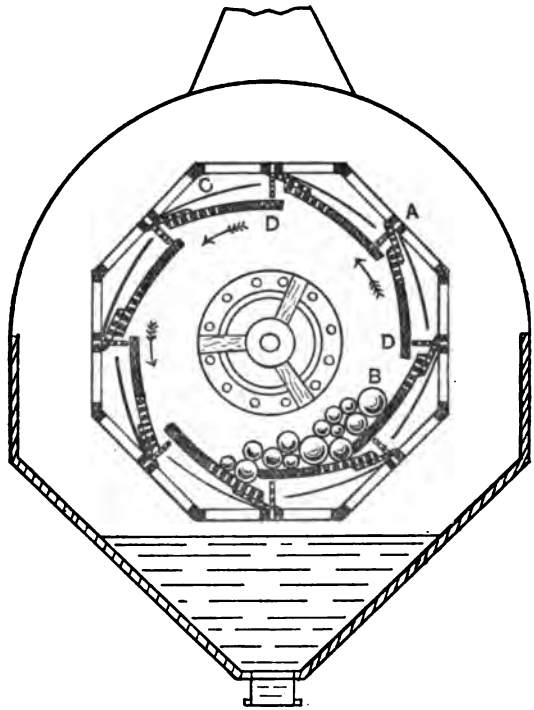


Fig. 22.—Ball grinding mill.

A, Drum; B, steel balls; C, sieves; D, iron plates.

This substance is more readily soluble in saline solutions—*e.g.*, ammonium citrate—than is $Ca_3(PO_4)_2$, to which the fact that basic slag is more efficient as a manure than mineral phosphate is, may be attributed. The slag is, however, of little value as a manure

unless it be very finely ground—*e.g.*, 80 per cent. of it should pass a sieve having 100 meshes per linear inch. The attainment of this condition constitutes the preparation of the slag for the market, and is expensive on account of the hardness of the material. Grinding is commonly performed by a ball mill shown in Fig. 22, which consists essentially of a drum, A, the inner surface of which is polygonal; the drum contains a number of balls of cast steel, B, of various sizes. Rotation of the drum breaks up the slag by the rolling and percussive action of the balls, and the comminuted material is systematically separated by sieves, C, in the sides of the drum. The sieves which effect the final separation are protected from direct contact with the balls by the perforated iron plates shown at D.

Bones.—These are of manurial value mainly on account of their phosphates, but they also contain nitrogenous matter unless a previous extraction has taken place. The average composition of dry bones is—

	Per cent.	
Fat, . . .	6	
Nitrogenous matter,	28	
Mineral matter, .	66	consisting of $Ca_3(PO_4)_2$, 56 per cent.; $CaCO_3$, 8 per cent.; $Mg_3(PO_4)_2$, 1 per cent.; CaF_2, 1 per cent. = 66.
	100	

Fresh bones contain about 3·7 per cent. of nitrogen; they decompose very slowly when used as manure. When the bones are previously fermented in heaps, the nitrogenous matter becomes more readily assimilable.

Bone Meal.—Bones are also more available as manure when they have been steamed for the removal of fat (see *Destructive distillation*, Vol. II., p. 103). Boiled bones which have passed through the glue-makers' hands (see *Glue*, Vol. II., Chap. XVI.) contain a smaller proportion of nitrogen (1·4 per cent. N) than do raw bones. The boiled bones can be more finely divided than is represented by the condition of bone meal; the fine product is known as **bone flour.**

Dissolved bones is the product of the treatment of bones with sulphuric acid. **Bone ash** is much imported from South America, and is used for making high-grade superphosphates, which contain about 75 per cent. of soluble phosphate. Comparisons made between the four phosphatic manures which have been described, show that they are available in the first year according to the following ratio:—

Superphosphate, ...	100
Finely-ground basic slag, ...	61
Steamed bone meal, ...	10
Ground coprolite, ...	9

It must be remembered that such portion of phosphatic manures as is not used in the first year is available subsequently.

(B.) **NITROGENOUS MANURES.—Ammonium Sulphate.**—This is obtained as a bye-product in the destructive distillation of coal. Its preparation has been described in the section on gas manufacture, p. 76. Pure ammonium sulphate contains 21·21 per cent. N, corresponding with 25·75 per cent. NH_3, and is a colourless salt. The commercial product varies in colour from grey to brown, owing to the presence of tarry matter, and is sometimes yellowish from the presence of As_2S_3; this body is formed by the action of the H_2S from the gas liquor on the arsenic present in the sulphuric acid in which the ammonia was absorbed. Commercial ammonium sulphate usually contains about 24·5 per cent. of ammonia. It should be free from ammonium sulphocyanide, which is a plant poison. This impurity is rarely present, save when the ammonium sulphate has been made by the direct saturation of gas liquor with sulphuric acid. **Soot,** which contains ammonium sulphate from the nitrogen and sulphur of coal, is also used as a manure. It contains on an average 4·2 per cent. NH_3.

Nitrate.—Sodium nitrate is obtained from the deposits of crude nitrate in Chili and Peru. The deposits, which lie about 6 to 10 feet below the surface, are known as **caliche,** and form a layer 4 to 6 feet deep. It is associated with clayey substances, and is stated to contain the following constituents:—

Sodium nitrate,	21·01	per cent.
Sodium chloride,	55·27	,,
Sodium sulphate,	4·74	,,
Calcium chloride,	0·33	,,
Potassium iodide,*	0·87	,,
Aluminium sulphate,	9·81	,,
Magnesium sulphate,	5·93	,,
Insoluble matter,	2·04	,,
	100·00	

The composition is, however, very various, and the content of sodium nitrate may reach 50 per cent.

The caliche is broken in a stone breaker, and systematically lixiviated in tanks heated by closed steam. (Water being a rare commodity in nitrate districts, it has to be used for repeated extractions.) When the liquid reaches a specific gravity of 1·55, it is run into crystallising vats, in which it remains from four to six days; the mother liquor is then run off, and used for the obtainment of iodine (see Vol. II., Chap. XVIII.). The nitrate deposited, after having been sun-dried, has the following composition (*Buchanan*):—

* The iodine characteristically present in crude nitrate probably exists as iodate; some of the chlorine is also present as perchlorate.

$NaNO_3$, ...	96·75 per cent.
NaCl, ...	0·75 ,,
Na_2SO_4, ...	0·30 ,,
Insoluble matter, ...	0·10 ,,
Water, ...	2·10 ,,
	100·00

Organic Nitrogenous Manures.—Dried blood obtained from slaughter-houses is a type of these. It contains from 9 to 12 per cent. N. Ground hoofs and horns form another manure of this class, as also waste woollen material—*e.g.*, shoddy (5 to 8 per cent. N) for manuring hops.

Before nitrogen in ammonium sulphate or organic substances can be taken up by a plant, it must be converted into a nitrate. The nitrogen in organic substances is chiefly in an albuminoid form. The first decomposition which such substances undergo results in the production of ammonia. The oxidation necessary for the conversion of ammonia into nitric acid is dependent upon the presence of a so-called "nitrifying" organism, which is a bacillus to which the name *nitromonas* has been provisionally assigned. The organism requires the usual mineral constituents —*e.g.*, phosphates—for its growth, and free access of air, on which account it is not active in the ground at a greater depth than 6 feet. Nitrites, instead of nitrates, are produced by it when its activity is sufficiently impaired. In order that all the ammonia may be converted into nitric acid, a fixed base must be present, otherwise ammonium nitrate is the final product. The temperatures between which the organism can act are 3° and 55° C. = 37° and 131° F., 37° C. = 99° F. being that at which it is most active. Darkness is favourable to its development. The process of nitrification is but one phase of the general oxidising action which is associated with the growth of this bacillus. Thus it is capable of converting iodides into iodates. "Denitrifying" organisms appear also to exist in the soil, capable of reducing nitrate even to free nitrogen. These become active when the soil is water-logged, and are inimical to plant life.

The process of nitrification is so rapid that ammonium sulphate is scarcely less readily assimilated than is sodium nitrate. There is, however, a certain amount of difference in the quality of certain crops when manured with nitrate and ammonium sulphate respectively, which will be found set forth in books on the subject. Another difference in their action is on the soil itself; before the nitrification of ammonium sulphate can be completed, the sulphuric acid must be removed by a base—*e.g.*, lime—in the soil, and a further quantity of base will be required by the nitric acid when formed.

The comparative slowness with which nitrogenous organic manures are taken up, is due to the necessity for their previous

conversion into ammonia during the process of decomposition. An advantageous effect of nitrate is its stimulating action upon growth, enabling plants to resist conditions unfavourable to the healthy attainment of maturity. It has become questionable whether crops cannot obtain the nitrogen which they require from the free nitrogen of the air. This certainly occurs with leguminous plants, upon the roots of which nodules containing micro-organisms are developed, which appear to be capable of converting nitrogen from the air in the pores of the soil into an assimilable form.

The nitrogen in ammonium sulphate, and that in nitrate, has about the same commercial value, which is not much higher than that for the most easily decomposable organic nitrogenous substances. The nitrogen in bones is of considerably lower value.

(C.) **POTASH MANURES.**—Potash, a necessary constituent of plant food, is supplied as one or other of the products obtained in the Stassfurt industry (see *Potash*, Vol. II., Chap. XVIII.). The chief salts used are kainit ($K_2SO_4 . MgSO_4 . MgCl_2 . 6H_2O$), which contains some 70 per cent. of the pure mineral, corresponding with 13 to 14 per cent. K_2O; the double sulphate of potassium and magnesium (27 to 28 per cent. K_2O) obtained from kainit; canallite ($KCl . MgCl_2 . 6H_2O$, with about 11 per cent. K_2O in the crude mineral); and crude potassium chloride of strength corresponding with about 50 per cent. K_2O. Magnesium salts and chlorides detract to some extent from the manurial value of these substances. Where timber is abundant, wood ashes are used containing 5 to 10 per cent. K_2O.

(D.) **GENERAL MANURES** are valued for their content of nitrogen, potash, and phosphates.

Farm-yard manure, the excrement of cattle, mixed with straw, may be regarded as the natural general manure, for it serves to return to the soil much of the plant food removed by the crop on which the cattle are fed. Since immature animals utilise more of the ash constituents of fodder than do full-grown animals, the composition of the manure depends upon the age of the stock; it also varies with the character of the food. Farm-yard manure is generally heaped, when it undergoes fermentation and much carbonaceous matter is dissipated as CO_2, CH_4, &c., and on that account the manure becomes concentrated to some extent.

Rotten farm-yard manure will contain 65 to 80 per cent. H_2O and 2·5 to 3 per cent. of true ash—*i.e.*, exclusive of earth and sand. It contains from 0·4 to 0·65 per cent. N, 0·4 to 0·7 per cent. K_2O, and 0·2 to 0·4 per cent. P_2O_5. The nutritive constituents of the animal excrement and that in the litter (straw) are both included in the above figures. The nitrogen of the urine being in the form of urea, uric acid, &c., is more readily available than that in the solid excreta.

Sewage and Products therefrom.—The application of human excrement as a manure is largely practised, particularly where it is customary to keep the excrement concentrated or merely diluted with an absorbent and deodorant—*e.g.*, earth or peat. Where the system of water-carriage is in use, the extreme dilution of the excrement renders it possible only to apply the sewage by the process of irrigation. The composition of human excrement is not essentially different from that of farm-yard manure; its amount may be gathered from the following table, which gives the average quantities per head per year:—

	Dung.	Urine.
Total quantity, . .	107 lbs.	1,063 lbs.
Dry matter, . .	24½ ,,	50¼ ,,
Nitrogen, . . .	1¾ ,,	9½ ,,
P_2O_5, . . .	1½ ,,	1½ ,,
K_2O, . . .	¾ ,,	1¾ ,,

The total value of these constituents is about 8s. 6d. per head per year.

The utilisation of sewage by irrigation requires that a large expanse of light absorbent soil shall be available for the reception of the sewage, its oxidation and its assimilation by plants. Although precipitation of sewage (by means of lime and other substances) is practised, the large quantity of precipitant necessary renders the resulting sludge valueless as manure.

When excrement is collected by the "pail system," without dilution, it can be treated with sulphuric acid, dried and disintegrated for use as manure, the product being known as **poudrette.**

Guano.—This is the excrement of sea birds in a more or less altered condition. A distinction is drawn between nitrogenous and phosphatic guanos; the former are either of recent origin, or have not been subjected to weathering, which is the case in such dry climates as that of Peru; the latter (found in Australasia) have been so washed by rain as to contain little or no nitrogen. The manurial composition of the two classes is shown below:—

	Nitrogenous. Per cent.	Phosphatic. Per cent.
N, ...	7·5	0·4
P_2O_5, ...	14·5	35·6
K_2O, ...	3·4	0·2

Dry Peruvian guano contains its nitrogen in the form of uric acid and urates; when these have undergone partial decomposition, the guano becomes damp and contains ammonium carbonate, to fix which a "dissolved" guano is made by treatment with sulphuric acid, the ammonia being converted into ammonium sulphate and the calcium phosphate rendered soluble. An "equalised" guano is a Peruvian guano in which the percentage of phosphates has been brought up by suitable admixture.

The pressed cake made in crushing rape seed for oil (*rape-cake*), being of little value for cattle food, is sometimes used for a general manure. Other similar cakes are also employed. The nitrogen varies from 4 to 7 per cent.; P_2O_5, 1·5 to 3·0 per cent.; K_2O, 1 to 2 per cent.

CHAPTER V.

PETROLEUM.

PETROLEUM, or mineral or rock oil, or "naphtha," is essentially a mixture of hydrocarbons of the paraffin and olefine series, the one or the other predominating according to the source of the oil. The range of homologues* is exceedingly wide, comprising even gases such as CH_4 and ethylene, C_2H_4, and solid hydrocarbons such as those constituting paraffin wax—for example, triacontane, $C_{30}H_{62}$, and melen, $C_{30}H_{60}$.

(A.) **ORIGIN AND DISTRIBUTION.**—Petroleum occurs in strata which consist largely of loose-textured conglomerates and sandstones (oil sands), its mode of distribution being similar to that of water in porous strata. In places it exudes at the surface of the earth, forming natural oil springs, but it is obtained in quantity by boring wells which tap the strata. Frequently, the oil is under such pressure from the gas associated with it that, when the superincumbent strata have been pierced, the oil gushes out in a fountain with great violence. Fountains of this character have occurred naturally for all historical time. The nature of the origin of petroleum is unknown. Various theories have been advanced. The most noteworthy of these are:—(1) That it is derived from the action of water on strongly heated iron carbide contained in the interior of the earth, such water having penetrated through crevices formed during volcanic eruptions. The chief support for this view is obtained from the fact that petroleum generally occurs at the foot of mountain chains. This theory was propounded by Mendeléeff after a personal study of the Caucasian oil-bearing district. (2) That it is a product of the decomposition of animal remains at a high temperature and pressure. Engler is responsible for this view, which is supported by direct experiment on the distillation of animal fats under pressure. The small quantity of nitrogen found in petroleum militates against the credibility of this explanation, but it is possible that the nitrogen may have been removed by a natural distillation of the oil (the nitrogen remaining with the residue) from its original source to the position in which it is found.

* It may be noted that, in chemical classification, those compounds which increase in molecular weight by the addition of CH_2 form an homologous series. This increase in molecular weight is accompanied by an approximately constant alteration in physical properties—*e.g.*, melting point and boiling point; both these rise as the series ascends.

(3) That it has been formed by the decomposition of the remains of marine animals in contact with saline deposits, and the subsequent resolution of the adipocere (the more permanent fatty constituents) into hydrocarbons and free CO_2. The fact that salt invariably accompanies petroleum lends credence to this hypothesis, which is due to Zaloziecki.

Petroleum is very widely distributed, but the bulk of that used comes from Pennsylvania or Baku. Other sources of minor importance are the deposits in Galicia, Canada, and British India.

(B.) **THE WINNING OF PETROLEUM.**—The copious outbursts of petroleum that characterised the earlier stages of the industry (which in its present size and manner of working is comparatively recent, dating from about 1860) are now relatively rare, and the oil is won by sinking bore-holes (about 6 inches in diameter), which are often of great depth—*e.g.*, as much as 2,400 feet and upwards. The method of sinking consists essentially in drilling a bore-hole to a depth of 200 to 300 feet by the use of a "drive-pipe," which is a steel tube with a cutting edge driven vertically downwards by a "maul." When the top part of the well is thus made and lined, the drilling proper begins. This consists in pounding the rock with a bit fixed at the end of a string of rods slung to a cable attached to a derrick—in order to allow of the string of tools being drawn up and suspended on occasion—and actuated by a beam-engine by which a reciprocating vertical motion is given. When a sufficient amount of the rock has been thus disintegrated, the tools are hung up by the derrick, and the detritus, which is suspended in the water that has trickled in, is removed by running down an iron tube fitted with a plunger and a valve, the apparatus being termed a sand pump. The well is lined with iron tubing as far as possible, the main object being to keep out the water that would otherwise find its way in. In the case of wells that do not flow spontaneously, an oil pump (which is simply a force pump driven from above) is let down and the oil thus brought to the surface. The oil is frequently accompanied by natural gas at a pressure of 400 to 500 lbs. per square inch, the gas consists chiefly of methane and hydrogen. The following may be taken as the average composition of the gas from the Pittsburg district:—

Methane,	67·0 per cent.
Hydrogen,	22·0 ,,
Ethane,	5·0 ,,
Nitrogen,	3·0 ,,
Ethylene,	1·0 ,,
Oxygen,	0·8 ,,
Carbon monoxide,	0·6 ,,
Carbon dioxide,	0·6 ,,
	100·0

Some wells yield oil containing a little gas in solution, others oil accompanied by much gas, and a third class gas exclusively. The gas is largely used as a fuel and for lighting in the districts where it is obtained, and, by imperfect combustion, for the production of a black pigment, "diamond black," or "carbon black" (*q.v.*).

(C.) **TRANSMISSION.**—On account of the wells of any one oil-bearing district being scattered, it is found economical to collect the oil to central storage tanks and thence to the refineries on the sea coast by means of long pipe-lines, a pressure of about 1,200 lbs. per square inch being used in this transmission. The trunk lines of pipes are 6 inches in diameter, and deliver the oil through branches to the refineries on their course. The pipes are kept clean by an iron scraper forced along by the flow of the oil.

(D.) **REFINING.**—The refining consists essentially in fractional distillation and treatment of the distillates with sulphuric acid and caustic soda to remove impurities. The method adopted depends to some extent on the percentage of the more volatile portions, and whether it be desired to produce the maximum yield of illuminants. The difference between the yield of the various fractions of Russian and American petroleum is shown by the following figures:—

	Russian.	American.
Petroleum spirit, . .	4	25
Illuminating oil, . .	39	60
Lubricating oils, . .	32	15
Residue and loss, . .	25	
	100	100

In America the distillation is not continuous, and is carried out in a crude oil still and a tar still, the oil being distilled in the first until the petroleum spirit and burning oils have come over, when the residue is transferred to the tar still, the distillate from which furnishes paraffin wax and lubricating oil. The crude oil stills are either horizontal steel cylinders 30 feet by 12 feet 6 inches in diameter, or of the "cheese box" pattern 9 feet in height and 30 feet in diameter, with a dome-shaped top. Both stills are fired direct, and steam is blown in to aid distillation. When the maximum quantity of illuminants is required, the upper part of the still is exposed to the air, in order that the heavier portions of the oil may condense and drop back into the hotter part of the still and thus be "cracked"—*i.e.*, decomposed into lighter hydrocarbons. When, on the other hand, lubricating

oils are required, this cracking is avoided, and the lighter portions are distilled over first to obtain a residue of "reduced oil" used for lubrication. In this case a vacuum is maintained in the still, and the use of superheated steam is substituted for direct firing. The tar still is a cylindrical vessel about 20 feet in length and 8 feet in diameter, and is heated finally to redness to get the full yield of oil. With both the crude oil and tar stills the condensers are essentially worms immersed in tanks through which cold water is circulated in the case of the former, and hot water in that of the latter, the hot water being necessary to prevent stoppages from the setting of the paraffin wax. In the distillation from the crude oil still, two main distillates are produced—(1) the "benzine* distillate," and (2) the "illuminating oil." The former is redistilled by steam heat, and the following fractions may be prepared from it:—

(1) **Cymogene**, which is essentially the gas butane, C_4H_{10}. This fraction is either burnt under the stills, or condensed by cold and pressure to a liquid boiling at 0° C. = 32° F., and having a specific gravity of 0·59. It is used in ice-making machines.

(2) **Rhigolene.**—This is also gaseous when first distilled, and consists mainly of pentane and iso-pentane, C_5H_{12}. It is condensed by cold to a liquid which boils at 18° C. = 64° F., and has the specific gravity 0·625. It is used as an anæsthetic, for driving gas engines, and for the pentane standard lamp (see *Valuation of coal gas*, Vol. I., p. 68).

(3) **Petroleum ether** or **gasolene** containing hexane and iso-hexane, C_6H_{14}, and boiling about 60° C. = 140° F.; its specific gravity is about 0·66. This is employed as a solvent for caoutchouc and oils, and is used for carburetting gas and preparing "air gas"—*i.e.*, air laden with a combustible vapour.

(4) **Naphtha** or **ligroïn**, consisting of the next few homologues of the paraffin series, boiling point 80° to 110° C. = 176° to 230° F., specific gravity about 0·700, used for burning and as a solvent for oils and resins.

(5) **Benzine** a slightly heavier fraction, boiling up to 150° C. = 302° F., specific gravity 0·740 and used as a turpentine substitute.

With respect to the fractional separation of these products, the same remarks that were made with regard to the fractionation of the distillate from coal tar (see Vol. II., p. 77) apply. The last and largest fraction, amounting to 40 per cent. of the whole, is sometimes deodorised by treatment with 0·5 per cent. of strong sulphuric acid in a vessel provided with a paddle agitator.

The illuminating oil distillate, coming over between 150° and 300° C. = 302° and 572° F., is submitted to treatment with

* This trade name must not be confounded with "benzene," which is the systematic name of the hydrocarbon, C_6H_6, obtained from coal tar.

sulphuric acid (about 2 per cent.), with which it is agitated by a stream of air, for as long as the temperature rises. After settling, the acid liquor is drawn off, and a water spray is made to percolate through the oil until the issuing water is no longer acid. The oil is then agitated with 1 per cent. of caustic soda solution, specific gravity 1·09, and, preferably, finally washed with water. The use of the sulphuric acid is to remove the bulk of the olefines as sulphonic acids, while the caustic soda is employed to remove such of these acids as are dissolved in the oil. The refined oil is known as **kerosene**, and is valued by its colour and flashing point. The former varies from pale yellow "standard white," to colourless, "water white," and the latter from 75° to 120° F. = 24° to 49° C. In this country the flashing point is determined by the "close test" made in the Abel apparatus. By "close test" is meant the method of ascertaining the temperature at which the oil evolves sufficient vapour to yield an explosive mixture with air in a closed vessel of standard dimensions.

The Abel apparatus consists of a water bath, in which is an "oil cup" (containing a fixed quantity of the oil to be tested), and provided with a cover having a slide in the lid so arranged that it can be opened at intervals and a small flame introduced into the vessel. The oil in the vessel is heated by the water bath and its temperature is ascertained by a thermometer. The legal minimum for the flashing point of kerosene is 73° F. = 23° C., corresponding with 100° F. = 38° C. by the obsolete "open test," which was conducted in an uncovered vessel. Scotch burning oils of good class rarely flash below 100° F. (close test), a much preferable limit.

The working up of the residue of the crude oil distillation in the tar still, produces a first runnings (20 to 25 per cent. of the contents of the still), which is turned back to the crude oil tank, or is treated and purified as a heavier grade of burning oil. The remaining distillate constitutes the **paraffin oil**; this is agitated with vitriol (5 per cent.) in agitators kept hot by steam jackets, then with water and caustic soda, and chilled by a freezing machine, when it becomes semi-solid from the separation of paraffin wax, and is pressed between sacking, the oil which drains away being used for lubrication. The wax is again pressed at a higher temperature to refine it (see *Shale oil*, Vol. II., p. 102). The bulk of lubricating oils is, however, obtained from "reduced oil" (*v.s.*). "Vaselene" is a product from such oils prepared by the separation of paraffin wax and filtration through animal charcoal; the first runnings from the filter are colourless and semi-solid when cold. It melts at 40° to 50° C. = 104° to 122° F., according to its grade. Spurious vaselene is made in Germany by dissolving paraffin wax in heavy hydrocarbon oil.

Lubricating oils from petroleum are characterised by their fluorescence or "bloom." They are generally deodorised and

decolorised by filtration through animal charcoal, and are often "de-bloomed" by the addition of various substances—*e.g.*, turmeric, nitronaphthalene, and picric acid. This treatment is only adopted when it is designed to substitute mineral for fatty lubricants without risking detection at sight. After the lubricating oils have distilled over, a semi-solid distillate is collected, technically known as "yellow wax;" it contains anthracene and similar hydrocarbons; when added to the lubricating oil it increases its density and raises the apparent yield of paraffin wax. The coke left in the still is about 12 per cent. of the charge.

The refining of petroleum in Russia, at Baku, is conducted in horizontal cylindrical stills, and the process is often continuous, in which case the stills are connected by pipes in groups of fourteen or more, and are heated to the temperature at which the product proper to each still comes over. By this plan a constant flow of petroleum (which is previously heated in a separate vessel by contact with the residues from the stills, produced by a previous operation) can be maintained, and the whole of the portion of the oil fit for burning is obtained from one or other of the stills, the last and most highly heated being no hotter (300° C. = 572° F.) than is consonant with the production of burning oil. The refining of the burning oil resembles the method used in America (*v.s.*). Heavier grades of burning oil than those made from American petroleum are prepared at Baku —*e.g.*, **solar oil** and **astralene**, specific gravity 0·850 to 0·880; flashing point, astralene 50° C. = 122° F., solar oil 80° C. = 176° F. —but their use is mainly confined to Russia, where they are given fiscal advantages. The residual oil from these stills (**astatki**) (specific gravity, 0·900 to 0·910) is mostly used as fuel for the stills themselves, for steam-raising on the works, for locomotives and marine engines on the local railways, rivers and seas, and for metallurgical operations. The principle of the method of burning consists in spraying the oil, by means of a jet of steam, into the furnace, the parts immediately in contact with the flame being protected with firebrick to preserve them from local overheating. Petroleum residues have about one and a-half times the heating power of an equal weight of coal, but the cost of carriage prevents it in competing with coal in this country except for special purposes (see Vol. I., p. 57).

A considerable quantity of the residue after the separation of the kerosene is, however, further distilled for lubricating oils, in smaller stills—sometimes worked by the continuous method already described, with the aid of superheated steam—until the distillate has the specific gravity of about 0·920. The distillate is then fractionated, and the first and second fractions (specific gravity 0·865 and 0·875), which are too light for lubricants, are sold for gas making, &c., and the remaining oil is collected in three fractions, forming three grades of lubricating oil, known respec-

tively as spindle oil (specific gravity 0·885 to 0·895), machinery oil (specific gravity 0·895 to 0·910), and cylinder oil (specific gravity over 0·910). Other, intermediate grades are prepared, which differ according to the design of the maker. These oils are purified by acid and alkali in a manner similar to that used for kerosene. A kind of vaselene is made from the residue in the still by returning one-third of its weight of the first fraction (specific gravity 0·865), and continuing to distil with superheated steam.

Russian petroleum, as opposed to American, is generally very poor in paraffin wax (0·25 per cent.), and this substance is not worked up. The absence of paraffin wax makes Russian lubricating oils better than American of the same grade, as they have less tendency to solidify on cooling.

By destructive distillation, astatki yields 30 to 40 per cent. of tar, containing 15 to 17 per cent. of 50 per cent. benzol. On destructively distilling the residual tar after the benzol is removed, 70 per cent. of a second tar is obtained, containing 7 to 10 per cent. of 50 per cent. benzol, 16 per cent. of naphthalene, 2 to 3 per cent. of 30 per cent. anthracene, and 24 per cent. of pitch. There is also a good deal of gas of high illuminating power (five times that of coal gas).

In instituting a chemical as distinct from a technical comparison of petroleum from Russian and American sources, a large difference is at once visible. Thus, American crude oil consists almost wholly of paraffins of the general formula C_nH_{2n+2}, whereas Russian oil is composed of olefines (C_nH_{2n}) and naphthenes ($C_nH_{2n-6}H_6$). The paraffins are more stable than the unsaturated hydrocarbons characteristic of Russian petroleum, and are less liable to be attacked in the process of refining. The olefines readily form addition products, and are easily sulphonated, but the naphthenes, being addition products of ring hydrocarbons, containing as many hydrogen atoms as can be combined with the nucleal ring, are unable to form addition products provided the ring structure remain undisturbed. Under suitable conditions, however, the naphthenes of Russian petroleum can be oxidised—*e.g.*, by a current of air in the presence of caustic soda—and then yield acids which unite with the alkali essential for their production. It has been proposed to take advantage of this formation of soap-like salts, in order to convert Russian petroleum into a semi-solid fuel without the addition of soap from an external source (see Vol. I., p. 58).

Ozokerite.—Ozokerite is a mixture of solid hydrocarbons, the composition of which corresponds with the formula C_nH_{2n}; it is regarded as an oxidation product of the hydrocarbons of crude petroleum, from which some hydrogen has been eliminated as water. It varies in consistency from a soft buttery mass to a

hard rock-like material generally black in colour. The largest deposits are found in Galicia. Its specific gravity varies from 0·85 to 0·95, and its melting point from 58° to 100° C. = 136° to 212° F. It occurs in veins 40 to 80 metres deep, which generally run through clay containing petroleum. The mining operations consist in sinking a shaft from which galleries are run along the veins. Gas occurs in the workings, and safety-lamps have to be used. The mineral is brought to the surface both in the form of lump and as earth containing ozokerite. The larger lumps can be melted for the refinery, while the earth is extracted by elutriation and the residues are boiled with water; recently it has been proposed to extract the last traces with light petroleum. The process of refining consists in treatment of the crude wax with fuming sulphuric acid, which converts some of the hydrocarbons into sulpho-compounds, and afterwards with charcoal to decolorise it. The material is then known as **ceresin**, and amounts to 60 to 70 per cent. of the crude ozokerite. It has a melting point of 61° to 78° C. = 142° to 172° F., and is largely used for the manufacture of candles (see Vol. II., Chap. XI.) and the adulteration of beeswax. There is also made an insulating material (**okonite**) which consists of a mixture of ozokerite and indiarubber.

Asphaltum.—This is the most condensed form of petroleum. Deposits of it occur in many countries, but the most noteworthy is that at the pitch lake of Trinidad. Asphaltum is a black material, varying from a very viscous fluid to a hard resonant rock; at Trinidad two kinds are obtained, the better being known as "Lake Pitch," the other as "Land Pitch." The former is soft, bituminous, and impregnated with gas, chiefly H_2S and CO_2. The latter appears to be lake pitch altered by oxidation, and is harder and free from gas. The following table shows the composition of typical samples, free from water:—

	Lake per cent.	Land per cent.
Inorganic matter (ash), .	36·56	37·74
Organic matter, not bitumen,	10·57	10·68
Bitumen, ...	52·87	51·58
	100·00	100·00

Both qualities, as dug, contain about 27 per cent. of water.

Although so similar in composition (stated in the proximate form adopted above), these kinds differ considerably in qualities; lake pitch, when refined, softens at 180° to 192° F. = 82° to 89° C., and flows at 189° to 210° F. = 87° to 99° C., while the corresponding numbers for refined land pitch are 190° to 237° F.

= 88° to 114° C., and 210° to 255° F. = 99° to 124° C. respectively.

The process of refining consists in heating the pitch in stills to drive off the water and to allow the mineral matter to deposit; the refined product is known locally as "epuré" or asphalt. The specific gravity of the refined lake asphalt is 1·38, that of land asphalt is 1·43.

The bulk of the asphalt obtained is used for paving, for which purpose it is heated with heavy paraffin oil, and this product, "asphalt cement," mixed with sand and other mineral matter, and applied while hot. "Asphalt Rock"—*e.g.*, Val de Travers asphalt—is a substance similar to Trinidad pitch, but containing up to 90 per cent. of mineral matter which is either siliceous or calcareous; when used for paving it is mixed with rich native asphaltum, such as Trinidad pitch, to increase the proportion of bituminous matter, the product being called "mastic."

CHAPTER VI.

LIME AND CEMENT.

LIME is always prepared industrially by the dissociation of calcium carbonate. This raw material occurs naturally in the following forms:—

(1) **Marble.**—A crystalline calcium carbonate nearly pure when white, sometimes containing mineral and carbonaceous (in black marble) colouring matter. The cost and closeness of texture of marble prevent its use as a raw material for making lime.

(2) **Limestone.**—This is a dense form of calcium carbonate, seldom so nearly pure as marble, generally containing silica, silicate of alumina and magnesium carbonate. When this last-named constituent is present to the extent of 5 per cent., the limestone may be termed dolomitic, and when 23 per cent. is present may be ranked as **dolomite**; typical dolomite corresponds with the formula $CaCO_3.MgCO_3$, the magnesium carbonate, therefore, amounting to 45·66 per cent. Dolomites are harder and better building materials than are limestones, being less easily attacked by an acid atmosphere (see Vol. I., p. 6); the mixture of lime and magnesia produced by burning dolomite is only used as a basic lining for furnaces (see Vol. I., p. 145). The variations in the composition of limestone may be judged by the following analyses:—

	Typical Pure Limestone.	Magnesian Limestone.	Hydraulic Limestone.
CaO, ...	55·54	27·22	44·84
MgO, ...	0·22	16·85	1·15
CO_2, ...	43·68	37·62	33·70
H_2O, ...	0·06	1·79	2·86
SO_3, ...	0·02	..	0·16
Insol. siliceous matter,	...	13·57	13·02
Combined silica, .	...	...	2·03
Al_2O_3, . . .	...	1·39	1·04
Fe_2O_3, . . .	...	1·56	1·00
	99·52	100·00	99·80

(3) **Chalk.**—Chalk is a less massive form than limestone of calcium carbonate, and varies in purity in the same manner. Ordinary chalk as quarried contains as much as 25 per cent. of water intermixed with it. The following analyses show the composition of two typical chalks used for lime and cement making:—

	Grey Chalk (yielding a somewhat hydraulic lime).	White Chalk (yielding a "fat" lime).
Moisture,	17·39	19·03
Sand and clay,	4·85	0·93
Combined SiO_2,	0·78	0·43
$Fe_2O_3 + Al_2O_3$,	0·53	0·48
$CaCO_3$,	73·84	76·60
$MgCO_3$,	0·66	0·88
Alkalies, organic matter, and loss,	1·95	1·65
	100·00	100·00

In general, carbonate of lime approximately pure will yield "fat" quicklime on burning, while, when siliceous and clayey constituents are present, a "poor" lime which slakes slowly and is more or less hydraulic is produced.

Principles of Lime-burning.—When calcium carbonate is heated under ordinary conditions, it begins to dissociate at about 400° C. = 752° F., but the dissociation does not proceed far unless the carbon dioxide be removed from the neighbourhood. Indeed, in a closed space, at a temperature of 1,020° C. = 1,868° F., calcium carbonate can be fused in the atmosphere of CO_2 generated by its partial decomposition; the resulting product has the aspect and physical properties of marble. The necessity for removing the carbon dioxide diminishes as the temperature rises; thus at 812° C. = 1,494° F. it may be allowed to accumulate until its pressure is 760 mm.—*i.e.*, one atmosphere. In practice the removal of the CO_2 is effected by the natural draught of the kiln, for in this manner the pressure due to CO_2 is reduced, since much of the total atmosphere consists of other gases. Although in a lime kiln the temperature may exceed 812° C. = 1,494° F., and dissociation would be completed without the draught, yet the process of burning is much accelerated by removal of CO_2 in this way; the removal is also imperative, because CaO and CO_2 would otherwise reunite (in the presence of water vapour) as the temperature fell. It is obvious from these facts that the dilution of the atmosphere of the kiln by an inert gas like steam will favour the decomposition of the calcium carbonate. The heat of formation of calcium carbonate from CaO and CO_2 is 42·5 Cal., whence it follows that 5·25 kilos. of fuel, having a heat of combustion

equal to that of carbon, should suffice for burning 100 kilos. of $CaCO_3$. In practice this quantity of fuel is much exceeded.

Kilns for Lime-burning.—It will be seen from what has been said above that the conditions for successful lime-burning are a temperature not lower than 812° C. = 1,494° F. and a rapid draught of inert gases through the heated limestone. Many forms of lime kilns are in use, but they are reducible to two types—(*a*) that in which the calcium carbonate is in contact only with the products of combustion, being separated from the fuel itself, and (*b*) that in which the calcium carbonate and fuel are mixed. The former yields a better lime, inasmuch as it is not contaminated with ash, while the latter is more economical of fuel and can be more readily adapted for continuous running.

(*a*) **Kilns in which the Fuel is not in contact with the Calcium Carbonate.**—One of the simplest forms is shown in Fig. 23. An egg-shaped firebrick kiln is filled with limestone supported on an arch roughly built of blocks of the same material. The fuel is placed below the arch, and the products of combustion pass upwards through the limestone, which is thus heated to the required temperature and converted into quicklime. Such a kiln only admits of discontinuous burning, and has to be charged for the next batch. The limestone may be supported above the fuel by other means—*e.g.*, a rough grating of iron bars, &c. The product is known as "flare-lime." The process of burning lime without solid fuel is obviously one that should be well adapted for performance by the aid of the gas producer. The arrangement generally adopted consists of an annular kiln (Fig. 24), the space in the centre of which, A, serves for storing the limestone, so that it may be charged into the surrounding kiln at a fairly high temperature. The gas from a producer passes through flues in the walls of the kiln, and the air for its combustion is admitted by a channel at the bottom of the annular space, B, B, and meets with the producer gas at a point about one-fourth of the height of the kiln, C, C, where the true lime-burning begins, the quantity of lime below this point serving to heat the air thus admitted.

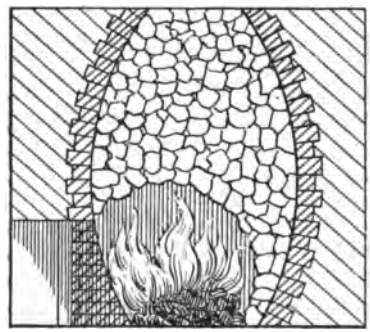


Fig. 23.—Lime kiln.

(*b*) **Kilns in which the Fuel is in contact with the Calcium Carbonate.**—The simplest form of kiln of this type is cylindrical, or like an inverted cone in shape, with a side opening at the

bottom, fed from the top with mixed limestone and fuel, and emptied below through the side opening. The process can be carried on continuously, the charging at the top and unloading beneath proceeding regularly. The consumption of fuel is about 25 per cent. of the limestone burnt, but the product is necessarily mixed with the siliceous ash of the fuel, its value being thereby

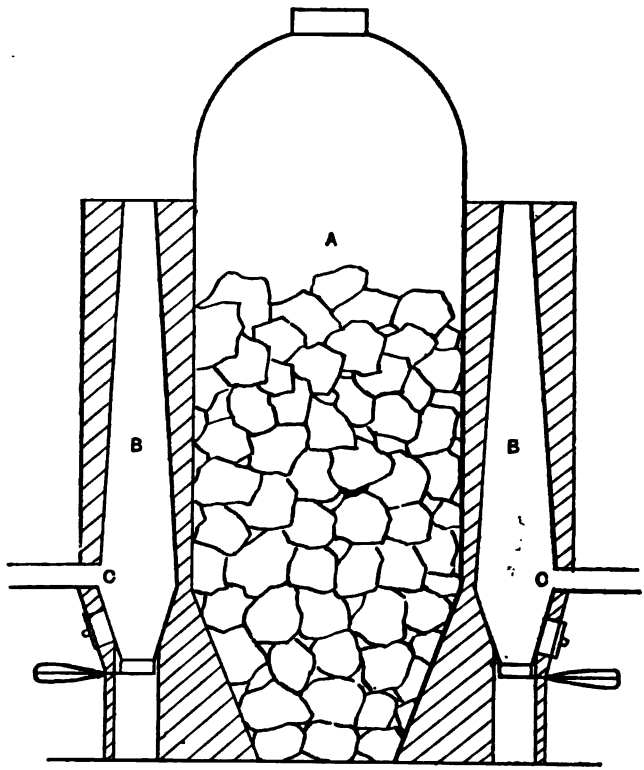


Fig. 24.—Lime kiln heated by producer gas.

B, B, Annular kiln; C, C, inlets for secondary air.

impaired. Other forms of kiln, in which the fuel and calcium carbonate are in contact, are the Hoffmann ring kiln and the Dietzsch stage kiln (*Etageofen*).

Lime.—The quality of the lime produced depends, as already stated, upon (1) the quality of the limestone, and (2) the nature of the ash of the fuel with which it has been burnt, assuming the systems mentioned in the last paragraph to have been used. Commercial lime of good quality contains 85 to 90

per cent. of free CaO, the remainder being calcium carbonate left unburnt or re-formed by exposure to air, calcium hydroxide (from absorption of moisture after burning), and calcium silicates and aluminates produced by the action of the lime on the siliceous constituents of the limestone and fuel ash. Magnesia is also commonly present, and when occurring in as high a proportion as 25 to 30 per cent. it renders the lime useless for ordinary purposes; the slowness of the hydration of the magnesia causes such lime to slake feebly and imperfectly. Technical terms are used to distinguish the qualities of commercial lime; thus "fat" lime is lime containing a minimum of foreign matter, and slaking rapidly and violently to a smooth pasty mass of "slaked" lime. Good fat lime slakes with so large and rapid an evolution of heat that the temperature of the mass may rise as high as 150° C. = 302° F. "Poor," or "over-burnt," or "dead-burnt" lime is that which slakes slowly and with little evolution of heat, and yields a slaked lime less smooth and plastic than that formed by fat lime. The more siliceous and clayey matter a limestone contains, the more liable it is to be over-burnt, and to yield a poor lime. As the reaction between the lime and the siliceous matter (producing calcium silicates and aluminates, which become hydrated slowly and with little evolution of heat) only takes place at a comparatively high temperature, the production of poor lime from limestones containing these constituents may be avoided by cautious burning.

Slaked lime dissolves in water, the solution containing 1 part of CaO in 780 parts of water at 15° C. = 60° F. Its solubility diminishes as the temperature rises, being rather less than half the above value at the boiling point. When lime is exposed to the air it becomes slaked by absorption of moisture, but there is *pari passu* an absorption of CO_2. Such air-slaked lime approximates to the composition $CaCO_3.Ca(OH)_2$.

Mortar.—Common mortar (as distinct from cement mortar) consists of 1 part of slaked lime and 3 of sharp sand (the proportions being generally by measure), and enough water to make a paste. One measure of fat lime will yield from 2 to 3 measures of slaked lime, while 1 measure of hydraulic lime yields 1·3 to 1·7 of the slaked product. The principles upon which the setting of mortar depends will be understood from what follows. When freshly slaked lime is allowed to dry it sets to a hard mass, which, however, is considerably smaller in volume than the wet lime, and, therefore, forms shrinkage cracks. Admixture with sand prevents this. This first stage or "setting" depends on the general property of very finely-divided amorphous substances, such as kaolin, of drying to a hard caked mass. This change takes place with lime, and then a further stage ("hardening") occurs, due to the absorption of CO_2 from the air, the mortar becoming coated with the calcium carbonate, the insolubility

of which makes the mortar permanent under ordinary weather conditions. In thick walls access of air is so slow that uncarbonated lime remains in the interior for many years.

The general effect of low temperatures upon mortar and cement during their application is to retard or prevent their setting. This fact is the cause of the abandonment of building operations during frost. Urgent work with cement in cold climates is conducted by the aid of steam heating at the point where the freshly mixed cement has been placed in position.

Besides its use as mortar, lime is employed in all chemical industries as the cheapest form of alkaline substance.

Plaster of Paris.—This material may be taken as a simple example of cements which set by hydration. It is manufactured by heating gypsum, $CaSO_4.2H_2O$, to a temperature of 120° to 130° C. = 248° to 266° F. This must be done out of contact with fuel, as the local heat of the burning particles that would be mixed with the gypsum (1) causes complete dehydration to $CaSO_4$, which is not plaster of Paris (*v.i.*), and (2) allows of the reduction of $CaSO_4$ to CaS, where the gypsum is in direct contact with carbonaceous matter. The gypsum is piled over arched fire-places, either in a rectangular chamber or in an egg-shaped kiln. Good plaster corresponds with the formula $2CaSO_4.H_2O$, complete dehydration only occurring at 194° C. = 381° F., when $CaSO_4$, which is but slowly acted on by water, is obtained. The mechanism of the setting of plaster of Paris may be understood from the following facts (*Le Chatelier*):—

When plaster of Paris ($2CaSO_4.H_2O$) is shaken with water, some of it is immediately dissolved. This portion then combines with water, becoming $CaSO_4.2H_2O$, which, however, is less soluble than $2CaSO_4.H_2O$, so that crystals of the former hydrate are deposited, and more $2CaSO_4.H_2O$ is dissolved by the same water. The process repeats itself until the whole quantity of calcium sulphate has crystallised in the form of $CaSO_4.2H_2O$. Obviously, when the water is only sufficient to make a cream or paste with the plaster, this cycle of reactions will convert the paste into one composed of crystals of $CaSO_4.2H_2O$, which, being needle-shaped and interlaced, constitute a coherent mass. Theoretically, about 13 per cent. of water, reckoned on the weight of the plaster, is necessary for its setting, but in practice at least 35 per cent. of water is used, as otherwise the setting is unmanageably rapid. Anhydrous calcium sulphate will set when mixed with water, but more slowly than plaster of Paris, becoming much harder than the latter. When gypsum is mixed with a small proportion of alum, and completely dehydrated, it sets more slowly than plaster of Paris, but less slowly than pure $CaSO_4$. Other salts—*e.g.*, borax—have been used for the same purpose. The mode of action in these bodies, which are present in the finished substance in inconsiderable quantity, has not

been satisfactorily elucidated. A mixture of lime with a small proportion of calcium sulphate constitutes Scott's cement. **Stucco** is plaster of Paris set with a solution of size; it is capable of receiving a polish.

Hydraulic Cements.—Hydraulic cements differ from common lime mortars in that they are not dependent upon desiccation for their setting, nor on carbonation for their hardening. Their setting depends upon hydration, analogous to that characteristic of plaster of Paris (*v.s.*). They are distinguished from plaster of Paris by their insolubility in water, which is sufficient in the case of "hydraulic" cements—*e.g.*, Portland cement—to allow of their use for structures immersed in water, such as docks and breakwaters.

Hydraulic Lime.—This material is manufactured by burning limestone containing siliceous and clayey matter. True hydraulic lime contains but little alumina, the silica being so finely divided and evenly distributed as to combine with the lime on burning with the aid of but little fluxing material (Al_2O_3 and Fe_2O_3)—(see *Portland cement*, Vol. II., p. 139). Thus, lime made by burning, the famous Theil limestone (found at Ardrèche in France) has the following composition :—

CaO,	74·0 per cent.
MgO,	0·7 ,,
SiO_2 (combined),	21·7 ,,
Sand,	0·3 ,,
Al_2O_3,	1·8 ,,
Fe_2O_3,	0·6 ,,
SO_3	0·3 ,,
CO_2 and H_2O,	0·6 ,,
	100·0 ,,

Limestone, yielding hydraulic limes, which are in common use in this country, are less typical than the example quoted above, as they contain clay which gives rise to the presence of an appreciable quantity of alumina in the lime produced. Thus, blue lias limestone has the following composition, an analysis being also given of a lime produced from a limestone of this class :—

Limestone.	Per cent.	Lime.	Per cent.
$CaCO_3$,	71·55	Insoluble residue,	2·39
$MgCO_3$,	1·35	Combined SiO_2,	14·17
Al_2O_3,	3·52	Al_2O_3,	6·79
SiO_2,	20·10	Fe_2O_3,	2·34
Fe_2O_3,	2·20	CaO,	63·43
Alkalies,	0·78	MgO,	1·54
Water and loss,	0·50	SO_3,	1·63
		CO_2,	3·64
		H_2O,	2·69
		Alkalies and loss,	1·38
	100·00		100·00

The reactions which take place on burning a limestone of this character consist in the attack of the siliceous and clayey matter by the lime, resulting in the formation of certain silicates and aluminates of lime (see *Portland cement*, Vol. II., p. 139); these remain mixed with some free lime for the saturation of which sufficient acid constituents (SiO_2 and Al_2O_3) are not present. In actual practice the free lime takes no essential part in the setting, and may be conveniently slaked by the cautious addition of water, insufficient to hydrate the cementitious silicates and aluminates, before the hydraulic lime is put on the market. This is the custom in France where large quantities are used, but in this country the lime is generally sold unslaked, and water sufficient for the slaking and setting added at the time of use. This is undesirable, as perfect slaking of all free lime should be secured before the material is used as a cement, lest slaking after partial setting should occur and give rise to disruptive strains. Good hydraulic lime serves much the same purposes as Portland cement (*q.v.*), and though not possessing the strength of the latter, is a useful and cheap material of construction. It has the advantage, moreover, of setting slowly, and remaining plastic for a sufficient time to allow the slight settlement, inevitable in much new work, to occur and terminate before the joints of the structure become rigid.

Roman Cement.—This cement is made by burning marl or any mixture of calcium carbonate and clay containing about 25 per cent. of the latter.

Septaria Nodules, consisting of chalk and clay in the above proportions, are dredged on the Kent and Essex coasts, and burnt to Roman cement. The temperature of burning is below the "clinkering" point (see *Portland cement*, Vol. II., pp. 135, 138), which is characteristic of complete union of the lime with the acid constituents. Roman cement is reddish in colour, and has a specific gravity of 2·5 to 3·0. On mixture with water it sets rapidly, and can be used as a true hydraulic cement—*i.e.*, to withstand the action of water. In its behaviour as a cement it is similar to, but weaker than, Portland cement. The following is an analysis of Roman cement:—

SiO_2,	19·26 per cent.
Insoluble residue,	5·11 ,,
Al_2O_3,	13·24 ,,
Fe_2O_3,	7·68 ,,
CaO,	45·36 ,,
MgO,	2·63 ,,
SO_3,	1·97 ,,
CO_2,	3·06 ,,
H_2O,	0·95 ,,
Alkalies and loss,	0·74 ,,
	100·00 ,,

Portland Cement.—Portland cement is the most important of hydraulic cements, and its nature and behaviour are in many respects typical of all cements which depend for their action on the changes which cementitious silicates and aluminates of lime undergo on admixture with water. It may be defined as a material produced by heating, to a clinkering temperature, an intimate mixture of calcareous, siliceous, and aluminous constituents, and finely grinding the resulting clinkered mass.

Various raw materials may be used; the calcareous material may be nearly pure calcium carbonate, such as chalk or limestone, or it may contain siliceous and clayey matter constituting a marl; the siliceous and aluminous material may be a "poor" (*i.e.*, siliceous) clay, such as a river mud, or a marl rich in clay, or a gault clay—*i.e.*, one containing calcium carbonate. The proportions of these constituents must be so adjusted that whatever the raw materials may be their mixture shall contain about 75 per cent. $CaCO_3$, the remainder being clay richer in silica than is pure kaolin.

The manufacture is carried out in the following stages :—

(1) **Mixing the raw Materials.**—Two systems of mixing are in use. In the first, which is called the **wet process**, chalk and clay in the proper proportions are mixed with much water in a wash-mill, consisting of a circular basin, in which a vertical spindle carrying radial arms provided with rakes, rotates and beats up the raw materials to a thin "slurry." The slurry flows through a grating to large reservoirs termed "backs," where it settles. After subsidence, which occupies some weeks, the water is drawn off, and the slurry, still containing about 50 per cent. of water, is removed for drying and burning (*v.i.*).

By the second or **semi-dry process** the raw materials are mixed with sufficient water to form a paste (capable of flowing and of being pumped like a liquid), by means of a wash-mill similar to that used in the wet process. As no separation of coarse particles by elutriation and subsidence (such as is characteristic of the older, wet process) occurs in the semi-dry process, the slurry from the wash-mill is ground wet between millstones until no visible particles of chalk remain in it. Chalk is a more suitable raw material than limestone, as it can be washed to a slurry, whereas limestone must be first ground or burnt to lime before it can be mixed with the clay.

(2) **Drying the Slurry.**—The slurry produced by either of the above processes is dried by the waste heat of the kilns (*v.i.*), or by that of the coke ovens used in some works for coking the coal previous to burning the cement. It is pumped on to "floors" which are made of iron plates, between which the waste gases circulate, and dries into irregular cakes ready to be fed into the kilns.

(3) **Burning to Clinker.**—The dried, well-mixed raw materials

must be raised to a clinkering temperature, which is attained at almost a white heat. The simplest form of cement kiln is the ordinary bottle kiln, which is a bottle-shaped brick structure lined with firebrick, at the bottom of which a pile of brushwood and coke is placed to serve for kindling the charge, consisting of alternate layers of dried slurry and coke. The burning is discontinuous, and the consumption of fuel is about 40 per cent. of the weight of the clinker produced. The process is uneconomical, more modern kilns consuming a smaller proportion of fuel. The type of furnace known as a "stage kiln" (*Etageofen*) is much used abroad, though not in this country to any extent. As shown in Fig. 25, it consists of two vertical shafts placed back to back, and constituting separate kilns. The upper part, A, is not in the same vertical plane as the lower, B, but the two are connected by a horizontal chamber, C. The charge is introduced through the door, D, in the upper part of the shaft, where it is heated by the products of combustion from the lower part of the kiln. It is raked through the door, E, along the horizontal chamber, C, and falls into the lower part of the shaft, B, where the combustion attains the clinkering temperature, and the clinker being plastic tends to stick to the walls of the kiln. It is dislodged by an iron tool through the working doors, F, and falls into the chamber, G, where it is cooled by air entering at the grate, H. The consumption of fuel in a Dietzsch kiln is from 10 to 20 per cent. of the clinker produced. Its chief drawback arises from the tendency of the clinker to ball together and stick to the walls of the kiln in its passage from entrance to exit.

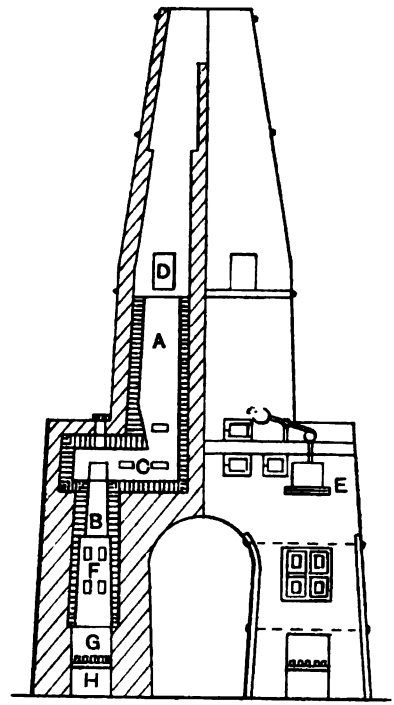


Fig. 25.—Stage kiln.

A, Upper part; B, lower part; C, connecting chamber; D, door for charging; E, F, working doors; H, grate.

What is probably the most economical form of kiln for burning

cement is the Hoffmann ring kiln (a plan of which is shown in Fig. 26), but it needs the shaping of the raw material into bricks or blocks, for a reason that will be stated later. For this purpose the bulk of the slurry is dried completely, and then mixed with the rest, so that the product may be kneadable; it is then shaped in a brick-making machine, and, if necessary, partly dried by a supplementary source of heat, the remainder of the drying being effected in the kiln. The Hoffmann kiln, as shown in the figure, consists of fourteen firebrick chambers, A, through the roof of which shoots, B, are arranged so as to distribute the fuel between the columns of blocks of cement to be burnt. Each

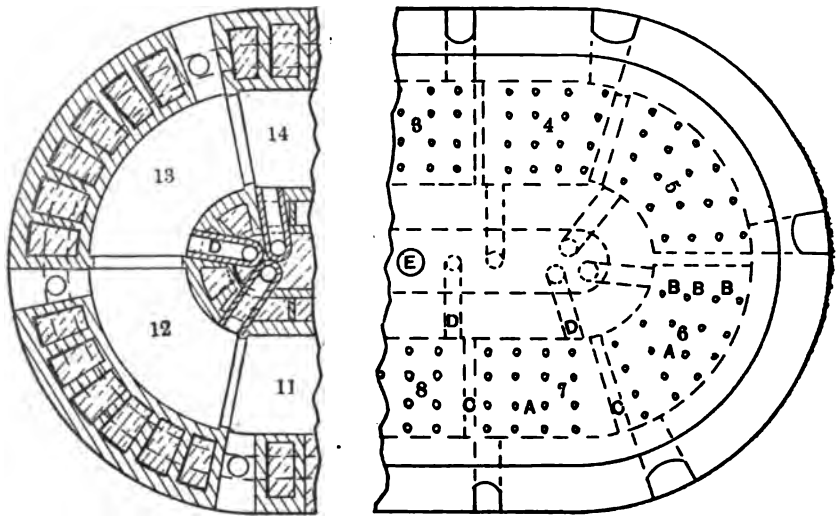


Fig. 26.—Hoffmann ring kiln.

A, Chambers; B, shoots; C, flue leading to chamber; D, flue leading to shaft; E, main shaft.

chamber is provided with a flue, C, leading into the next chamber, and also a flue, D, leading to the central main shaft, E. The working of the kiln is as follows:—Each chamber contains its complement of bricks. Taking the case where the bricks in chambers 1 to 5 have been burnt and those in 7 to 12 are being burnt, those in 13 are waiting to be burnt and those in 14 are being unloaded; No. 6, which is already hot enough to start combustion, is charged with fuel through the shoots, which are then closed. All flues to the central chimney except that from 12 are also closed, and the draught from No. 12 draws in air through the whole series from an opening in chamber 1; the air traverses these chambers full of hot clinker, becoming warmed

in its passage, passing from chamber to chamber by the flues, C. The products of combustion from 6 pass through the chambers 7 to 12, heating their contents and then escaping nearly cool by the central shaft. By this means the charges in these chambers are systematically raised from the ordinary temperature to one just short of clinkering. The diversion of the gases from 12 to the central flue is effected by a shield in the flue between 12 and 13. This shield is often of paper, so that when the temperature rises sufficiently, it burns through and automatically includes No. 13 in the series; the damper in the flue leading from 12 to the central shaft is then closed, and that in 13 opened. The contents of 6 is now thoroughly burnt, and 7 is charged with fuel, the whole series of operations being shifted on by one chamber, No. 1 (the most thoroughly cooled) being unloaded and the cold air allowed to enter through 2. No. 14, at the extreme end of the half of the set of chambers in the act of burning, is meanwhile filled with fresh bricks, and the cycle of operations indefinitely repeated.

The continuous drying and burning of cement have also been effected in cylinders capable of rotation about an axis set slightly inclined to the horizontal and fed by producer gas, but the system, which presents many advantages in principle, has not yet come into extended use.

Cement clinker being a highly basic material (*v.i.*) should not be burnt in an acid-lined kiln, although this is commonly done. An attempt to form a basic lining is often made by plastering the inside of the kiln with slurry. Recently, kilns have been lined with magnesia bricks, such as are used in steel furnaces, and a "neutral" lining of bauxite has also been employed.

(4) **Grinding the Clinker to Cement.**—Well-burnt clinker is in the form of dark brown or greenish-black lumps, so hard as to need much power for comminution. As cement is usually so finely ground as to leave little or no residue on a sieve having 2,500 meshes per square inch, the choice of a grinding plant is of much importance. The clinker is first reduced in size by a stonebreaker, after which the grinding proper takes place. Usually, in this country, French burr stones set horizontally are employed, with or without sieves to size the product and to prevent coarse particles finding their way into the finished cement. Edge-runners are also used, and, abroad, ball-mills are extensively adopted (see *Basic slag*, Vol. II., p. 110). It may be said that as finer grinding is demanded by the consumers of cement, more economical systems than that of grinding by ordinary mill-stones will come into general use. The ground cement is generally stored, and turned over to aërate and slake any small quantity of unsaturated lime which it may contain, before it is put to use.

(5) **Composition and Properties of Portland Cement.**—The fol-

lowing table of analyses gives the composition of typical samples of dried clay, slurry and cement (for chalk analyses see p. 127):—

	Clay.		Slurry.		Cement.
	Per cent.		Per cent.		Per cent.
Sand, . . .	28·42	$CaCO_3$, . . .	75·32	SiO_2, ...	20·68
Combined SiO_2,	30·32	Fe_2O_3, . . .	0·40	Insoluble residue	0·82
Al_2O_3, . . .	15·49	Al_2O_3, . . .	2·51	Al_2O_3, . . .	9·50
Fe_2O_3, . . .	7·74	CaO (not as $CaCO_3$), .	1·31	Fe_2O_3, . . .	4·06
CaO, ...	2·04			CaO, ...	61·96
MgO, ...	1·96	MgO, ...	0·41	MgO, ...	1·07
SO_3, ...	1·96	Sand and clay,	12·68	SO_3, ...	1·04
Combined water and loss,	12·07	Soluble SiO_2, .	3·23	$H_2O + CO_2$, . .	0·46
		Combined H_2O and loss, .	4·14	Alkalies and loss	0·41
	100·00		100·00		100·00

The fact that cement is generally burnt with coke containing 10 per cent. and upwards of siliceous ash, makes it necessary to use enough chalk to provide lime for the acid constituents of the ash; whence it follows that a slurry containing a suitable percentage of calcium carbonate for burning with solid fuel, would tend to yield a cement with an excess of lime if burnt with gaseous fuel. Variations in the content of ash and the quantity of fuel consumed, therefore involve variations in the composition of the slurry. Calculation of the composition of a cement from the known composition of the slurry from which it is made is, consequently, not exact unless the ash of the fuel be taken into account. The following is an outline of the chief reactions which occur in burning cement:—At a temperature of about 600° C. = 1,112° F. the clay is dehydrated, and at 800° to 900° C. = 1,472° to 1,652° F. the calcium carbonate is converted into caustic lime. A reaction then begins between the clay and the lime. Where the particles of lime and clay are in contact, fusible double silicates are produced, and serve as a flux to cause the union of the lime with the silica to form tricalcium silicate, which is the chief cementitious compound present in cement and is infusible *per se*, and calcium aluminates, which are fusible. The clinker of Portland cement is sufficiently basic to cause the ferric oxide of the clay to function, like the alumina, as an acid, and to form calcium ferrites. Completeness of reaction is never attained in practice, chiefly because it is impracticable to fuse the clinker, which is at most pasty, so that perfect commingling and consequent union of the acid and basic constituents are not attained. Local excess of acid constituents and local excess of basic constituents may occur in clinker, the mean composition of which is correct. It follows that clinker as drawn from the kiln

is a somewhat heterogeneous product. Three main materials can be distinguished therein. (1) Hard coherent dark clinker, containing tricalcium silicate ($3CaO.SiO_2$) as its essential constituent. (2) "Fallen" clinker or dust, resulting from the spontaneous disintegration of clinker containing deficiency of lime, and due to the presence of dicalcium silicate ($2CaO.SiO_2$) as the predominant constituent. (3) Underburnt clinker, yellow and pink in colour, in which complete reaction between the lime and clay has not occurred, and which contains free lime. To secure the best cement, only sound clinker should be ground, but it is usual to send all except greatly underburnt material to the crushers. It is probable that the fallen cement poor in lime and the underburnt portion containing free lime may, nevertheless, serve as cement by mutual action on mixing with water, the said action being analogous to that taking place between puzzuolana and lime (p. 140).

The important constituents of good cement are tricalcium silicate ($3CaO.SiO_2$), tricalcium aluminate ($3CaO.Al_2O_3$), and tricalcium alumino-ferrite ($3CaO.Al_2O_3.Fe_2O_3$). Besides these there are found as subsidiary constituents dicalcium silicate ($2CaO.SiO_2$), and monocalcium silicate ($CaO.SiO_2$); the former is remarkable for its change of state on cooling, for its crystals being twinned and contracting unequally at opposing faces, separate and thus cause any mass composed of it to fall to powder. It is the presence of this substance which induces the falling of cement. Sound cement contains no free lime (see Vol. I., p. 11).

The setting of Portland cement is in nature similar to that of other hydraulic cements (save slag cement and puzzuolana cement) and is essentially a phenomenon of hydration. The successive changes that occur on mixing Portland cement with water to form a paste are as follows:—(1) Loose compounds of lime—*e.g.*, calcium ferrites—slake and are decomposed; (2) tricalcium aluminate reacts with water and calcium hydroxide (this latter having been produced by the decomposition of tricalcium silicate (*v.i.*) and calcium ferrites) according to the equation—

$$3CaO.Al_2O_3 + Ca(OH)_2 + 11H_2O = 4CaO.Al_2O_3.12H_2O—$$

This causes the initial setting of the cement; (3) tricalcium silicate reacts with water thus:—

$$2(3CaO.SiO_2) + 9H_2O = 2(CaO.SiO_2).5H_2O + 4Ca(OH)_2.$$

The hardening of cement and the attainment of its characteristically great strength are due to this reaction. The products of hydration of the tricalcium aluminate and tricalcium silicate pass into solution, and subsequently crystallise from their supersaturated solutions thus formed, in a manner similar to that of plaster of Paris (p. 131). This explanation is confirmed by the observation that the temperature of the cement after gauging with

water does not immediately rise, but begins to do so after a few moments; the period of delay probably corresponds with that of dissolution, and the rise of temperature indicates the beginning of crystallisation. Commercial Portland cement of good quality should contain the maximum possible proportion of tricalcium silicate and tricalcium aluminate, but should have no excess of basic constituents. Its composition should, therefore, fall within the limits expressed by the equation—

$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} \leq 3$$

In this equation the quantities are expressed in equivalents, not in percentages. Its meaning is that the total basic constituents of any cement expressed in equivalents must be equal to or less than three times the total acid constituents also expressed in equivalents, so that after the formation of tricalcium silicate and tricalcium aluminate there may remain no base unsaturated. All methods of stating the ratio of acids to bases in terms other than equivalents are necessarily meaningless.

Puzzuolanic Cements.—Certain silicates decomposable by acids and partly soluble in alkalies, are sufficiently active to combine with slaked "fat" lime to form calcium silicates insoluble in water. In consequence of this property, mixtures of these silicates and lime have long been used as hydraulic cement. Such are:—

(1) **Puzzuolana.**—Puzzuolana is a volcanic tufa found largely in the neighbourhood of Naples and Rome.

The following are analyses of each kind:—

	Neapolitan.	Roman.
	Per cent.	Per cent.
Soluble silica,	27·80	32·64
Insoluble siliceous residue,	35·38	25·94
$Al_2O_3 + Fe_2O_3$,	19·80	22·74
CaO,	5·68	4·06
MgO,	0·35	1·37
SO_3,	Trace	Trace
$H_2O + CO_2$,	4·27	8·92
Alkalies and loss,	6·72	4·33
	100·00	100·00

(2) **Trass** is also a volcanic tufa, and is found in the Rhine district. Its composition is similar to that of puzzuolana.

(3) **Santorin earth**, from the Greek island of Santorin, is a substance of like character.

(4) **Blast furnace slag** is prepared by granulating a slag rich in lime—*e.g.*, containing 50 per cent. CaO, 30 per cent. SiO_2, 20

per cent. Al_2O_3. The granulation is essential, as if the slag be allowed to cool slowly and assume a crystalline state its chemical energy is decreased, and it combines but feebly with lime. The granulation is effected by allowing the molten slag to flow from the blast furnace into a trough of running water.

Cements are made from these materials by mixing them (preferably finely ground) with lime, in proportions varying from 1 : 1 of lime to 4 : 1 of lime. **Slag cement** is made on a considerable scale by mixing very intimately, in a ball-mill, finely-ground granulated blast furnace slag with about one-third its weight of slaked lime. It attains nearly as high a strength as Portland cement, but is usually slow in setting, taking 6 to 12 hours, this property being characteristic of cements of the puzzuolana class.

Artificial Stone.—The cheapness and great strength of Portland cement have led to its use in the manufacture of various kinds of artificial stone. Concrete (see Vol. I., p. 9) is a rough form of artificial stone, and the preparation of both materials is conducted on the same general lines—viz., the cementing together of an "aggregate" composed of fragments of natural stone by means of Portland or other suitable cement. The natural stone (*e.g.*, granite in the form of chippings) is mixed with cement mortar (*i.e.*, cement and sand), made into a plastic paste with water, and moulded into any desired shape. Such artificial stone is sometimes treated with a strong solution of silicate of soda (*water glass*)—(for the manufacture of water glass, *v.i.*). The effect of the sodium silicate is to react with the lime set free by the hydration of the cement (p. 139) to form calcium silicate, the caustic soda liberated being afterwards washed out. The strength of the stone is thus increased, and its porosity diminished. Where Portland cement is not a constituent of the stone, the materials may be mixed with water glass, and saturated with calcium chloride solution, calcium silicate and sodium chloride (the latter removable by washing) being formed.

Water Glass.—Water glass (*soluble glass*) is an alkali silicate, soluble in water. It is made by fusing silica, in almost any convenient form, with sodium or potassium carbonate. The addition of a little carbonaceous matter (*e.g.*, small coal) aids the reaction, possibly owing to a tendency towards the formation of Na_2O (or K_2O) by the oxidation of sodium (or K), liberated by the carbon. When sulphate is substituted for carbonate, the presence of carbon reduces the sulphate to sulphide, which acts freely on the silica. Finely-divided silica may also be heated with a solution of caustic alkali under pressure, for the same manufacture. The reaction is aided by transforming insoluble forms of silica, such as flints, into the more soluble variety by heating them to redness, and quenching in water. Commercial soluble glass varies between

the limits $Na_2O.4SiO_2$ and $Na_2O.2SiO_2$, the commonest grade being about $Na_2O.3SiO_2$, and is made by fusing 2 parts of quartz sand with 1 part of sodium carbonate and 0·1 part of small coal. The solubility varies inversely as the proportion of silica, a glass rich in silica being very sparingly soluble. Consequently, a large proportion of soluble glass is sold in solution, as the solid is often slow to dissolve. Soluble glass is decomposed by the feeblest acids, even CO_2, gelatinous silica being separated. Besides being used for making artificial stone, soluble glass is employed for rendering wood fire-proof, as a detergent, and for protecting natural stone of a quality that does not weather well.

CHAPTER VII.

CLAY INDUSTRIES AND GLASS.

CLAY INDUSTRIES.—Clay.—Typical pure clay is kaolin, $2SiO_2.Al_2O_3.2H_2O$, corresponding with the composition SiO_2 47·1 per cent., Al_2O_3 39·2 per cent., H_2O 13·7 per cent. Such typical clay results from the weathering of granite, a rock which contains a felspar (orthoclase, $K_2O.Al_2O_3.6SiO_2$, or albite, $Na_2O.Al_2O_3.6SiO_2$), a mica, generally potash mica, $K_2O.3Al_2O_3.4SiO_2$, and quartz. By the weathering process the alkalies are leached out, and the silicate of alumina is hydrated and washed away from the less finely-divided quartz. White granites which contain soft earthy felspar (see Vol. I., p. 3) are more easily weathered than those containing orthoclase, and yield an approximately pure kaolin. It will be seen that the purity of the clay resulting from this weathering process depends upon the composition of the parent rock, the perfection of the elutriation and the nature of other alluvial deposits with which the clay has become mixed. The following analyses show the composition of typical pottery clays containing much or little nearly pure kaolin :—

	Pure Kaolin (Zettlitz).	Kaolin with Quartz.	Kaolin with Felspar.
	Per cent.	Per cent.	Per cent.
Kaolin clay substance,*	96·6	63·8	55·9
Felspar, . . .	1·1	0·7	38·2
Quartz, . . .	2·3	35·5	5·9

* Containing—

	Pure Kaolin (Zettlitz).	Kaolin with Quartz.	Kaolin with Felspar.
	Per cent.	Per cent.	Per cent.
Silica, . . .	45·6	45·3	47·1
Alumina, . . .	38·1	37·1	36·0
Ferric oxide, . .	0·9	1·3	0·6
Lime, . . .	...	...	
Magnesia, . . .	0·7	0·8	3·3
Alkalies, . . .	1·8	2·0	
Water, . . .	13·3	12·1	12·9

Clays of all classes are fitted for their use in making pottery by two main properties:—(1) The ease with which they may be moulded and shaped when wet, and (2) their change of state to a hard unalterable condition when fired. The former of these two properties appears to depend on the mechanical condition of the clay rather than on its chemical composition. Pure kaolin is less plastic than are clays containing certain impurities—*e.g.*, free hydrated silica and ferric oxide. A comparison of the analyses of the clay substance of kaolin clays with those of the clay substance of eminently plastic clays, shows in the true clay substance (as distinct from quartz and felspar) of the latter class of clays, a slightly higher percentage of silica, ferric oxide and alkalies and a lower percentage of alumina and water. The change which clays undergo on heating is one of dehydration and agglomeration accompanied by much shrinkage. Pure kaolin is extremely refractory, being infusible at the temperature of the porcelain furnace. The general effect of impurities, especially of bases, is to lower the fusing point of kaolin. The effect is, however, not confined to bases; silica will also lower the melting point of kaolin by the formation of double silicates with such unsaturated bases as may be present in the kaolin as impurities. Further addition of silica (which is itself infusible at the temperature of industrial furnaces) will again raise the melting point. Equivalent quantities of bases lower the melting point in the following order:—K_2O, Fe_2O_3, CaO, MgO, the last-named having the greatest effect, for equal weights. The clays fall into the following classes, according to their chief industrial use:—

(1) **Porcelain clay** or **Cornish clay**, approximately pure kaolin, poor in plasticity, refractory, burning to a white or light cream colour.

(2) **Plastic clay**, more impure than the foregoing, more plastic and less refractory; it burns to a yellow-red colour, and is used for ordinary earthenware, and its commonest variety serves for brick making. Mixed with calcium carbonate it constitutes clay marls.

(3) **Fireclays.**—These are clays found chiefly in the coal measures which, so far as the true clay substance is concerned, approach porcelain clay in composition (though often containing more iron), but contain more silica as quartz. They are highly refractory, dark in colour, and are used for furnace linings and crucibles. The varieties, rich in quartz, form a link between normal fireclay and such highly siliceous substances as Dinas "fireclay" (with 97 to 98 per cent. SiO_2) and ganister, which are used for making specially refractory bricks.

Bricks.—Common bricks are made of the commoner kinds of clay, containing sufficient sand to prevent undue shrinkage on burning. The clay is weathered, and large stones and lumps of limestone, pyrites, &c., which would tend to disintegrate the

bricks after burning by slaking and oxidation, are removed, and the clay pugged to a smooth paste, moulded into a rectangular rod and cut into bricks. The raw bricks are burnt in heaps or clamps with small fuel, such as breeze, or occasionally in closed kilns—*e.g.*, the Hoffmann kiln (p. 136). The chief change produced by firing in the case of common bricks, consists in the dehydration of the clay and a sintering of the more fusible constituents. The colour of the finished brick depends on the percentage of iron present, the proportion of lime in the brick earth, and the intensity of the firing. At moderate temperatures a yellow or red brick is produced, while if lime be present (gault bricks) the tint is light yellow or cream colour, and, if the temperature of firing be high, a grey, blue or black colour results from the formation of magnetic oxide of iron. **Blue bricks** are made from a clay rich in iron, and containing more or less marl, and are fired at a high temperature. Usually a salt glaze (p. 149) is given to such bricks, which are also fairly sintered throughout, and are, therefore, tolerably impervious. **Glazed bricks** are made more carefully and of better materials than ordinary bricks, and after firing are glazed in the same manner as stoneware (p. 149), usually with lead glazes rendered opaque with stannic oxide. Firebricks are made from fireclays mixed, if necessary, with sand, and frequently with already burnt fireclay. Such an addition prevents the brick from cracking on exposure to sudden changes of temperature. The following analyses exhibit the differences between common brick earth and a good fireclay :—

Brick clay.	Per cent.
Quartz, . . .	16·42
Felspar, . .	3·27
Calcium carbonate,	4·45
,, sulphate, .	0·95
True clay substance,	74·91
Consisting of :—	Per cent.
Silica, . .	46·96
Alumina, .	36·42
Ferric oxide, .	2·80
Magnesia, .	0·87
Alkalies, .	0·91
Water, . .	12·04

Fireclay.	Per cent.
Quartz, . . .	84·59
Combined silica, .	5·11
Alumina, . .	5·40
Ferric oxide, .	0·21
Lime, . . .	0·20
Magnesia, . .	0·09
Potash, . . .	0·61
Water, . . .	3·74

The former contains numerous fluxing constituents—*e.g.*, lime, ferric oxide and felspar—while the latter is nearly free from such substances, and is accordingly refractory.

Tiles are made from clay suitable for bricks, but of rather better grade. They are burnt in kilns in the same manner as the better class of bricks. A mode of preparation which presents a certain economy consists in sifting the dried clay, slightly damping it by sprinkling, pressing the feebly coherent powder in a powerful press, and burning the raw tile thus produced. In producing tiles with coloured patterns (**encaustic tiles**) a layer

of the best clay is put on to a body of coarse clay, which is still further backed by a common clay. The face of the tile is pressed on to a plaster of Paris mould of the required pattern, and the indentations thus formed are filled with a slip consisting of clay mixed with the required colour, the tile thus ornamented being burned in saggers (p. 147) and glazed. Tiles are frequently glazed, the general methods being similar to those used for earthenware (p. 149).

Pure kaolin would be useless for making pottery, as its infusibility and large contraction on heating prevent its consolidating to a sound clinkered mass. The first drawback is met by the addition of some flux—*e.g.*, felspar—and the second by the admixture of an inert infusible aggregate, such as sand. The three main classes into which pottery can be divided are (1) **porcelain**; (2) **stoneware**; (3) **earthenware**. In the first, the body of the ware is clinkered throughout, and no hard line of demarcation exists between the glaze and the body of the ware. When thin it is translucent, and being made from the purest materials it is white. In the second, less pure materials are used, and the ware is coloured and opaque, but the body and glaze are similarly inseparable, and the body itself is impervious. In the third class, the body of the ware is pervious and presents no sign of sintering, and the glaze is adherent only, and not truly incorporated with the body of the ware.

Porcelain.—Hard Porcelain.—This is made from a mixture of kaolin, felspar and quartz, which must be ground, sifted and levigated. A mixture used for Berlin porcelain consists of 55 parts of true kaolin, 22·5 of quartz and 22·5 of felspar. The quartz is not added as such, being present in the kaolin used. The kaolin is made into a thin paste with water, the quartz (if needed) and felspar are ignited and quenched in water to disintegrate them, and also made into thin pastes, all three materials being mixed by pumping from one vessel to another, and then separated from the surplus water by filter presses, the resulting mass being in a kneadable condition. The plasticity of the paste is often improved by weathering; the cause of this improvement is imperfectly understood. The vessel to be made is fashioned either on a potter's wheel or by moulding—*i.e.*, by pressing the paste either in its moist form or after drying, powdering and slightly damping (so as to stick together), into suitable moulds, or by casting the liquid paste in a plaster of Paris mould, which absorbs the water, leaving a coating of raw paste. In this last case repetition of the process can be carried on until the desired thickness is attained. The ware, however prepared, is allowed to dry very slowly, and is given a first baking ("biscuit firing") at a moderate temperature (700° to 800° C. = 1,292° to 1,472° F.), whereby the kaolin is dehydrated and the goods become strong enough to bear handling. The ware is protected from dust and

direct contact with the flame in the kiln by being enclosed in "saggers," which are boxes made of refractory clay and built up in columns in the kiln. During the first burning the ware shrinks about 3 per cent. of its linear dimensions. When ordinary glazed, as opposed to biscuit, porcelain is to be produced, the ware after the first burning is dipped in a slip of similar composition to the body of the ware, but more fusible. Thus Berlin porcelain is glazed with a mixture of kaolin, felspar, quartz, gypsum or marble, and broken porcelain. A typical glaze of this class has the composition 10 SiO_2, 1 Al_2O_3, 0·7 CaO, 0·2 MgO, 0·1 K_2O (stated in equivalents). The materials for the glaze are reduced to an impalpable powder and made into a thin slip with water; the goods are dipped in this slip and retain a coating of the raw glaze, after which treatment they are dried and burnt a second time at a temperature of about 1,700° C. = 3,092° F., just short of the fusing point of platinum. During the burning, the body of the ware clinkers and the glaze fuses, so that the resulting porcelain is impervious throughout, and is not dependent upon the glaze for its impenetrability. A further contraction of 7 to 9 per cent. on the original linear size of the goods takes place during this firing. During burning, the ware is placed in "saggers" as before, care being taken that no glazed portion of the porcelain is in contact with the sagger, lest it stick. Similarly, to avoid strain, the clay of which the saggers are made must shrink in firing to the same extent as the goods burnt. A kiln frequently used consists of two cylindrical chambers, one above the other, at the bottom of each of which are several firing grates. Openings from these grates into the kiln permit of the passage of the flame to the goods stacked therein. Flues from the top of the lower chamber pass into the upper, and thence through the dome-shaped top of the kiln, which constitutes a third chamber kept at a lower temperature, this division being used for the first firing. The burning usually takes about twenty-four hours, and the goods are allowed to cool for three or four days before opening the kiln. The progress of burning is watched through spyholes, and the temperature judged by the behaviour of Seger's cones, which are small pyramids made of different porcelain mixtures of known softening point, forming a series covering the whole range of temperature in use in porcelain burning. The ultimate composition and approximate fusing point of a few of these cones (the full series comprising thirty-six numbers) are given below:—

No.					Fusing Point.
1	0·6 Al_2O_3 + 0·4 Fe_2O_3	8 SiO_2	1·4 CaO	0·6 K_2O	1,150° C. = 2,102° F.
10	1 Al_2O_3	10 SiO_2	0·7 CaO	0·3 K_2O	1,410° C. = 2,570° F.
20	1 Al_2O_3	10 SiO_2	1·18 CaO	0·08 K_2O	1,700° C. = 3,092° F.

Above this temperature, Al_2O_3 and SiO_2 alone enter into the composition of the cones, the ratio being 1 Al_2O_3 : 2SiO_2 (corresponding with pure kaolin) for the highest temperature. A similar series for the control of the firing of soft glazes, which contains B_2O_3 to lower the melting point, is also in use. In Berlin porcelain, as in other kinds still to be described, the composition of the glaze should approximate as nearly to that of the body of the ware as is consistent with the greater fusibility of the former. The contraction of the glaze during firing and its coefficient of expansion when finished, should be as nearly as possible identical with the same properties of the ware itself. It must "wet" the body of the ware and soak into it to some extent, so that no hard and fast line exists between them, and they are mechanically one.

Colouring Porcelain.—Only metallic oxides which yield coloured silicates are available for decorating porcelain. Coloured glazes may be regarded as the ordinary colourless glazes with one or more of the oxides of heavy metals replacing lime or alumina. If the oxide be of the type RO, it is substituted for an equivalent of lime, while if it be of the type R_2O_3, it replaces alumina.

For the colourations imparted by individual oxides, see *Glass*, Vol II., p. 158. The colouring of porcelain is done in one of two ways. In the first, the coloured glaze is applied to the biscuit ware before glazing with the ordinary colourless glaze, and the colour is thus protected in the finished ware. In the second method, a colourless glaze is first applied, and then fusible coloured glazes or enamels are painted on the surface of this, the whole being fired in a muffle at a temperature below the fusing point of the colourless glaze. In this case the colour is on the surface, and is unprotected.

Soft Porcelain.—All varieties of soft porcelain may be regarded as intermediate in composition and properties between hard porcelain and glass. Thus, the soft porcelain formerly made at Sèvres was prepared by mixing 80 parts of white sand, 22 of nitre, 7 of salt, 4 each of alum, gypsum and soda, and "fritting" the mass together until incipient fusion (**sintering**) took place. The **frit** was powdered, and 75 parts mixed with 17 of chalk and 8 of a calcareous marl, the whole being washed to a slip, moulded and burnt in the usual way. Unlike hard porcelain, soft porcelain receives its heavier firing the first time it enters the kiln. The subsequent firing to fix the glaze, which is a lead-alkali glass (see *Flint glass*, Vol. II., p. 158), is carried out at a lower temperature on account of the fusibility of the glaze. **English soft porcelain** is distinguished by the presence of calcium phosphate; a typical mixture consists of kaolin 27 per cent., China stone (a Cornish clay rich in felspar) 27 per cent., bone ash 46 per cent. The glaze is a lead glass or a glaze containing B_2O_3, and the firing is conducted as for French soft porcelain.

When a clay containing traces of iron is used, the yellow colour produced is corrected by the addition of a small proportion of oxide of cobalt to the paste. Soft porcelain is well adapted for ornamental purposes, but it is less resistant than hard porcelain, especially to rapid fluctuations of temperature, and the glaze is softer, and more liable to crack or "craze," as the formation of a network of hair cracks is termed.

Biscuit porcelain is the name given to unglazed hard porcelain. **Parian** is that used for unglazed soft porcelain, both materials being used for statuettes.

Stoneware.—Stoneware, like porcelain, is clinkered so as to be impervious, but its constituents have not been so near fusion as to yield a translucent ware. It consists of the same material as porcelain, but there is no typical soft variety—*e.g.*, one containing bone ash. A comparatively large proportion of felspar is used, and flint is a characteristic constituent, frequently amounting to half the weight of the mass. The flints are prepared by calcining and quenching in water (the silica undergoing molecular change), by which treatment they become easier to grind. Wedgwood ware consists of a clay, but slightly refractory, together with kaolin, flint, and China stone (*v.s.*). Stoneware is fired at a somewhat lower temperature than porcelain, and generally without the use of saggers. Owing to the imperviousness of the body of the ware, glazing is unnecessary, but for goods to resist corrosive liquids (*e.g.*, acid jars, bombonnes, cooling worms, &c.) a "salt glaze" may be employed. The process of salt glazing consists in throwing wet salt on to the fire at the end of the biscuit firing, whereby the salt is decomposed, and hydrochloric acid and soda result, the latter attacking the surface of the ware and forming soda glass thereon. It is obvious that such glazing is only applicable to ware which is rich in silica, this serving as an acid to unite with the soda. In addition to its ordinary uses, stoneware is employed for making hard refractory paving tiles, the fact that it is clinkered throughout adding greatly to its durability.

Earthenware.—This material is characterised by the fact that the body of the ware has at no time approached fusion. A typical paste for white earthenware consists of "ball-clay" (a highly plastic clay) 25 per cent., china-clay 32 per cent., flint 35 per cent., Cornish stone 8 per cent. In preparing the raw materials for such earthenware, magnetic iron oxide is removed by running the slip through a box containing magnets. The commoner varieties of earthenware are brown in colour, the iron of the clay not having been removed. Glazes for earthenware consist of mixtures of clay, sand, soda, borax and red lead. The chief firing takes place in the biscuit state, the second being at a lower temperature on account of the fusibility of the glaze. The glaze does not penetrate the body of the ware, and is

easily detachable therefrom—a distinction from stoneware and porcelain.

The common English kiln for firing earthenware and stoneware consists of a dome-shaped hood containing a circular oven with a bee-hive top. The flames from the fires, which are situated round the base of the oven, enter partly through flues running up the sides of the oven and partly underneath it; the wares are imbedded in sand or ground flint in saggers with which the oven is filled save for spaces to allow the circulation of the flame. Holes in the crown of the oven admit of the escape of the flue gases into the hood which creates the necessary draught and protects the furnace from weather. In modern practice regenerative gas-firing is much used, and the Hoffmann kiln (p. 136) is also employed to a considerable extent.

GLASS.—Glass is defined as a mixture of silicates, one of which is always the silicate of an alkali. It is amorphous, very difficultly attacked by water and acids, and usually transparent. No single silicate fulfils these conditions. The silicates of the heavy metals are usually coloured, and are, therefore, only used as constituents of coloured glasses. Most ordinary colourless glasses fall into two classes—viz., alkali-lime silicates and alkali-lead silicates—for these silicates, unlike most others, have but little tendency to crystallise on solidification. The mixture of silicates for glass making must be so chosen that it shall melt at a yellow heat * and be plastic at a temperature considerably below this. These conditions are fulfilled by mixtures rich in alkali silicates, but these are too easily attacked by water to be available as glass. Double silicates, free from alkali, are sufficiently resistant to water and acids, but need a higher working temperature than is convenient for glass making.

Most glasses correspond with the formula $3SiO_2 . RO$, where RO stands for both alkali and lime (or lead oxide). The alkali and lime (or lead oxide) vary in proportion from 1 : 1 to 5 : 7 (in equivalents), corresponding with the formulæ $Na_2O.CaO.6SiO_2$ and $5Na_2O.7CaO.36SiO_2$; in these formulæ K_2O may replace Na_2O, and PbO may replace CaO.

There are many varieties of glass—the chief of which will be described below—but the main raw materials, which fused together form glass, are comparatively few, and are included in the following list:—

Raw Materials.—(1) **Silica.**—This is now almost always quartz sand. For the best kinds of glass it must be as free as possible from ferric oxide, to remove which treatment with hydrochloric acid is sometimes practised. For commoner glass 0·5 per cent. Fe_2O_3 is permissible. In England, Lancashire and Bedfordshire sand is esteemed for glass making, and on

* For the temperatures corresponding with this and similar industrial terms, see Vol. I., p. 83.

the Continent deposits of great purity occur at Aix and Fontainbleau. Belgian sand is also much imported into this country. Quartz and flint are also forms of silica sometimes used. Whichever be adopted it is advantageous to heat to redness and quench in water to increase the ease with which the silica is attacked in the melting pot.

(2) **Alkali.**—Sodium carbonate free from iron, made by either the Leblanc or the ammonia process, is the chief form of alkali employed in glass making. The reaction between sodium carbonate and sand when fused together is represented by the following equation :—

$$Na_2CO_3 + 3SiO_2 = Na_2O.3SiO_2 + CO_2.$$

Sodium carbonate has, however, been considerably displaced by sodium sulphate, which, when needed especially free from iron, is crystallised in lead pans for the glass industry. The same salt obtained as a bye-product from the Stassfurt deposits, is also used. Sodium sulphate is decomposed by silica at a high temperature, thus—

$$Na_2SO_4 + 3SiO_2 = Na_2O.3SiO_2 + SO_3.$$

The reaction is facilitated by the addition of carbon, which reduces SO_3 to SO_2, CO_2 being simultaneously formed. It will be seen that 71 parts of sodium sulphate are needed to replace 53 parts of sodium carbonate. This and the higher temperature necessary, tend to reduce the advantage gained by substituting the cheaper sodium sulphate for sodium carbonate. The use of carbon must be restricted lest Na_2S be formed, which dissolves in the glass yielding a yellow or brown colour. A still cheaper source of soda for glass making would be salt, were it not that the volatility of NaCl and the fact that steam is necessary for its decomposition by SiO_2, have hitherto prevented its adoption on a manufacturing scale. Ordinary potash glass is made from crude carbonate of potash or wood-ashes, while refined potassium carbonate is used for the best grades. Potassium sulphate cannot well be substituted for the carbonate, as its decomposition in the manner practised for sodium sulphate takes place with difficulty.

(3) **Lime.**—Pure marble is used for the best glass, and limestone or chalk for the common kinds. Marls (containing clay as well as $CaCO_3$) are sometimes used, a portion of their alumina entering into the composition of the glass. Many siliceous minerals, especially such as contain alkali—*e.g.*, felspar—may be used for common bottle glass.

(4) **Lead oxide** is most frequently used in the form of minium (red lead, Pb_3O_4), more rarely as litharge (PbO); the excess of oxygen in the former is an advantage tending to prevent reduction of the metal; the latter is not only destitute of this excess, but frequently contains some metallic lead.

(5) **Cullet.**—This is the technical term for broken glass, which material acts as a flux, aiding the reaction between the constituents of the new glass, and thereby hindering loss of alkali by volatilisation. For fine glasses care must be taken that the cullet approximate to the composition of the glass to be made.

(6) **Correctives of Colour.**—These are of two classes, those which tint the glass with a shade complementary to that due to the impurities in the raw materials, and those which act as oxidising agents. Manganese dioxide, the best known of these additions has long been used under the name **glass maker's soap**, on account of its property of clearing away the green colour due to ferrous silicate in the glass. This it effects by oxidising the ferrous silicate to the slightly yellow ferric salt, and by yielding a violet manganic silicate complementary in colour to green ferrous silicate; thus it possesses a double function. Manganese dioxide for glass makers' use must obviously be free from iron. Titanic acid also effects chromatic neutralisation. Nickel oxide and cobalt oxide are other reagents of the same class. Zinc oxide removes the tint due to sodium sulphide by double decomposition with that body. Agents of the second or oxidising class are arsenious oxide (white arsenic)—which oxidises ferrous oxide, being itself reduced to metallic arsenic which volatilises—nitre and manganese dioxide, as indicated above.

The raw materials of whatever class are thoroughly ground, sifted, and mixed in proportions consonant with the character of the glass to be made. These proportions must be modified so as to allow for the loss of alkali which occurs by volatilisation, and the amount which is likely to be removed as *glass-gall* (*i.e.*, excess of sodium salts, chiefly sulphate, floating on the surface of the fused glass); the total deficit ranges from 10 to 20 per cent.

Fusion of the Raw Materials to Glass.—The older and still common method of fusing glass consists in heating it in pots of refractory clay set in a furnace fired by external grates—so that only flame and gaseous products of combustion may come in contact with the pots—or with gaseous fuel used in a regenerative furnace. According to more recent practice, the glass is melted in one large vessel or tank (instead of in several pots), the tank being set in a regenerative furnace very similar in construction to a steel furnace. With regard to the details of melting the following may be said:—

A glass-pot is circular, resembling a large flower pot, but, of course, without the whole at the bottom. It is from 3 to 5 feet in diameter, and of similar height. It is built up from fireclay, the best for the purpose being from Stourbridge, mixed with about one-fifth of its weight of old pots ground to powder. The ground pot is for the purpose of preventing shrinkage cracks when the new pot is fired, and its proportion varies with the quality of the plastic clay; thus Stourbridge clay with some 40 per cent.

of sand, being but little plastic and not greatly liable to shrinkage, needs a smaller proportion of ground pot than a plastic clay richer in clay substances, and correspondingly poorer in sand. The pots require very slow drying (in rooms warmed to about 25° C. = 77° F. for three to twelve months), and very gradual baking (lasting from 3 to 7 days). In order both to protect the pot, and to avoid contaminating the charge with matter from the pot, a glaze is applied by melting a charge of cullet (broken glass) in the pot, a crust of glass being thus caused to adhere to the walls. The life of a glass-pot (during which it must not be

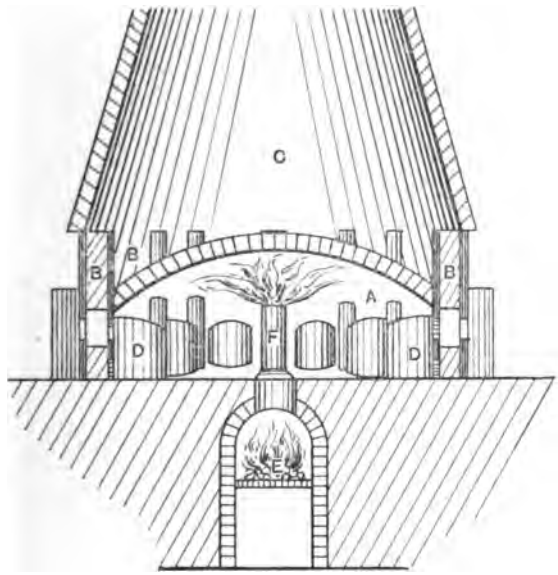


Fig. 27.—Glass Furnace (old type).

A, Furnace chamber; B, flues; C, hood; D, pots; E, firegrate; F, short flue.

allowed to cool) varies from a few weeks to nearly a year, according to the quality of its material and its conditions of use. A furnace of the older type without gaseous firing is shown in Fig. 27. The furnace itself, A, is a circular brickwork chamber with side openings which carry the flame and products of combustion through the flues, B, into the hood, C. The pots, D, are placed round the chamber, A, opposite openings in between the flue openings. The firegrate, E, is situated below the furnace chamber, and the flames and hot gases are carried up the short flue, F, so that they may strike upon and be reflected from the domed roof of the chamber. The reason for covering

in the space where the pots are heated is to prevent the soot and flue dust from falling back into the pots. In more modern practice the grate is charged from below, so that the products of each feeding of fuel may pass through the mass of heated fuel above it, and smoke be thus minimised. The furnace is fed with small coal, the depth of fuel is considerable, and there are air inlets both above and below the fuel, so that the grate becomes in effect a producer, and the firing is comparable with that of a furnace fed with producer gas. (Many pot furnaces are now fired by producer gas and worked in connection with regenerators.)

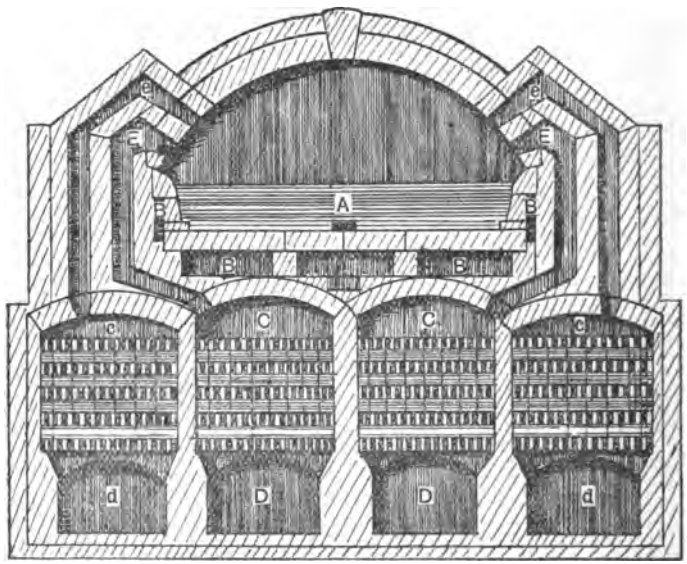


Fig. 28.—Siemens tank furnace.

A, Tank; B, B, air channels; C *c*, C *c*, regenerators; D, D, gas channels; *d*, *d*, air channels to the regenerators; E *e*, E *e*, hot gas channels.

Mechanical stoking is advantageous in that it avoids admission of a large volume of cold air, such as takes place every time a hand-fired furnace is stoked; the regularity of heating thus obtained is favourable to the life of the glass-pots, and to the quality of the glass.

In order to avoid the expense involved in the use of numerous glass-pots, difficult to build and of short life, and also to facilitate continuous working, the Siemens tank furnace is now largely adopted. It is shown in Fig. 28.

In the figure, A is the fireclay tank kept cool as to its walls by the circulation of air through the channels, B, B, B, B. The

regenerators, C *c* and C *c*, are worked in pairs as usual (see Vol. I., p. 67), the producer gas being supplied to them through the channels, D, D, and the air through the channels, *d*, *d*. The entrance of the heated gases to the furnace takes place through the channels E *e*, E *e*. The charge is introduced through the working door at one end of the furnace, and the finished glass is withdrawn at the other end, where the working platform is situated. To avoid the necessity of skimming the whole of the surface of the fused charge, a fireclay ring floats on the glass at the door where the molten "metal" is withdrawn; the function of this ring is to preserve a clean surface of glass within it, the glass-gall being prevented from entering, while the glass itself flows gradually up into the area enclosed by the ring as the upper layer is ladled out. The same purpose of freeing the glass from floating impurities and rendering it homogeneous, is served by transverse divisions of the glass tank provided with openings at their lower edges, so that the glass first fused at the far end of the furnace, where it is hottest, is forced to pass below one or more septa, and thus is skimmed and mixed, arriving at the cooler end uniform in texture and free from glass-gall. The tank can also be divided longitudinally, and several kinds of glass worked simultaneously in the same furnace.

In the case of the older pot furnace, when the pots are in work they are quickly charged with alternate layers of cullet and the mixtures of raw materials ("the batch"). The quantity of the charge is restricted, so as to prevent the semi-fused mass, vesiculated with SO_2 or CO_2, from frothing over. As the mixture melts, a further portion of the charge is added. When fusion is complete, decolorising and oxidising agents are added (p. 152); a scum of glass-gall collects on the surface, and is skimmed from time to time. After this "refining," the melt is sampled, when it should be found of good colour, free from lumps of unattacked silica, bubbles and striæ. In some twenty-four hours the glass is ready to be worked, and is ladled out.

Recently, an attempt has been made to improve glass after the fusion of its raw materials, by passing a stream of oxygen into it while in the furnace, with the double object of mechanical agitation and oxidation of residual impurities; a difficulty in effecting this has arisen from the ease with which leading tubes of most practicable materials are attacked by the fused glass; platinum cannot be used, as it lacks rigidity at the temperature of the glass furnace.

All the earlier methods of working glass depend on the use of the glassblower's pipe. Thus, in making hollow ware (blown bottles and flasks), a mass of "metal" (glass in a plastic state) is picked up on the end of an iron tube and blown into an elongated bulb, the shape of which may be modified by manipulation, or by the aid of a mould. For crown glass, a bulb is blown, opened

into a goblet shape, and extended to a sheet by rapid rotation. For sheet glass, a bulb is blown, rolled to a cylindrical form, cut longitudinally, and extended to a flat sheet on a clay plate. By more modern processes, in which the glass can be worked in large masses at a high temperature, common articles—*e.g.*, rough tumblers and salt cellars—can be pressed, the operation consisting in dropping plastic glass into metal moulds, and applying mechanical pressure. Facility in handling large quantities of fully-molten glass has allowed of the manufacture of plate glass by casting the fused glass on to a table, constructed of thick cast-iron plates arranged to form a horizontal bed, and passing a roller over it. A table thus constructed in segments is preferable to one made of a single plate, because such local arching as may arise from irregular expansion is distributed, and is at no point so great as would be the case with a single large plate; consequently, less waste is encountered in grinding the plate glass to a plane surface. Plate glass is ground flat and polished by fixing the plate on a bed of plaster of Paris and grinding it by means of cast-iron plates carried on arms which revolve on a central axis. The first grinding is effected by sand and water, and the final surface obtained by emery, rouge, &c.

Annealing and "Hardening" Glass.—All glass, if allowed to cool from the plastic state by direct exposure to the ordinary temperature, is liable to develop internal strains due to irregular solidification and consequent contraction. The strains may be so severe as to lead to spontaneous fracture. In consequence of this peculiarity, glass articles, from bottles to plate glass, are annealed in special ovens, either by passage on travelling bands through a long flue of gradually diminishing temperature, or by exposure while stationary to a temperature, short of fusion, which is lowered by degrees. When the cooling of a glass article is rapid, but uniform over the surface, the article is "toughened" and possesses greater mechanical strength than does annealed glass. Such toughened glass is prepared by plunging the red-hot goods into an oil bath, the temperature of which varies from 70° to 350° C. = 158 to 662° F. Although resisting shocks sufficient to break common glass, material prepared in this manner is in a condition of internal strain; when fracture actually occurs at one spot it determines the disintegration of the whole mass with almost explosive violence. An application of the same principle of rapid uniform cooling is found in Siemens toughened glass for street pavement lights, and similar purposes, which is made by casting glass into moulds of the same conductivity and heat capacity as the glass itself, reheating to the softening point of the glass, and allowing the glass and the mould to cool rapidly together.

Devitrification of Glass.—The object of ordinary glass annealing is to obtain the material free from internal strains,

but the heating needed to allow of the self-adjustment of such pre-existing strains must not be so prolonged as to permit that complete re-arrangement of the molecules of the material—viz., their orientation into the form of crystals—which indicates a state of equilibrium naturally acquired. The production of such crystals causes the glass to become opaque and porcelain-like, whence the name of **Reaumur's porcelain** for devitrified glass—the substance having been prepared as a substitute for true porcelain. The change is purely physical, no chemical alteration (such as loss of alkali) being observed; the glass can be restored to its vitreous condition by refusion.

The influence of rate of cooling on natural mixtures of silicates comparable with glass, is similar to that on glass itself. Thus, the slowly-cooled rocks, like granite, contain large crystalline individuals; more recent eruptive rocks, such as lava, are micro-crystalline, while silicates of the obsidian order, which have been very quickly cooled, closely resemble glass in structure. Granulated blast-furnace slag (Vol. I., p. 133) is another instance.

Typical Composition of Alkali-Lime Glass.—As already stated, both soda glass and potash glass (and glasses containing both alkalies) are made. There does not appear to be any great difference in the properties—*e.g.*, fusibility—of potash and soda glass,* though glasses containing mixtures of the two alkalies in equivalent proportions are more fusible than those with either alone.

The following are examples of ordinary glasses of the soda-lime class:—

	Soda Glass, Rich in Silica.	Combustion Tube, Bohemian Glass.	Soda Glass, Poor in Silica.
	Per cent.	Per cent.	Per cent.
SiO_2, . .	77·0	73·1	68·6
Na_2O, . .	15·5	3·1	17·7
K_2O, . .	...	11·5	...
CaO, . .	7·4	10·4	9·7
MgO, . .	...	0·3	...
$Al_2O_3 + Fe_2O_3$,	...	0·4	4·0
MnO, . .	...	0·5	...

Lead Glass.—This is a potash-lead glass, nearly free from foreign constituents, and approximates to a formula ranging from $K_2O.PbO.5SiO_2$ to $5K_2O.7PbO.36SiO_2$. Its freedom from iron causes it to be colourless, it exhibiting no green tint such as is characteristic of soda-lime glass. It has a considerable lustre, due to its high refractive index, which increases with the con-

*The refractory character of the "potash" glass, used for combustion tubing in the laboratory, appears to be due rather to its high content of silica than to the nature of the alkali.

tent of lead. Its comparative softness fits it for the manufacture of ornamental cut glass, which is fashioned by pressure against a wheel fed with emery, putty powder, &c. It melts at a lower temperature than soda-lime glass and is less easily devitrified. A typical mixture for producing lead glass is 300 parts of sand, 100 of potassium carbonate, 150 of red lead, and 50 of litharge. The ease with which the lead may be reduced (communicating a black stain to the glass) necessitates the use of a covered pot (Fig. 29). Lead glass is often termed **flint glass**, the name being especially applied to such as is prepared for optical purposes. The grades of lead glass richer in lead contain from 40 to 50 per cent. of lead oxide and are termed **strass**. Strass is used for the manufacture of imitation precious stones on account of its high refractive index. The softness of glass rich in lead affords an easy means of distinguishing false gems made of this material.

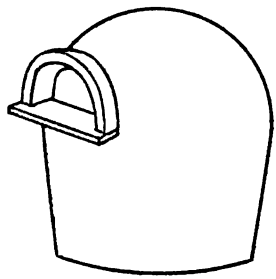


Fig. 29.—Pot for lead glass.

Coloured and Opal Glass.—Coloured glass is produced by the addition of the oxides of heavy metals to ordinary glass mixtures, each metal communicating a colour depending on its nature and condition of oxidation. The decoration and colouring of porcelain are effected by the use of silicate mixtures similar to coloured glasses. Some of the more important coloured glasses are described below.

Red glass.—Ruby-red glass is produced by adding about 1 per cent. of cupric oxide and 1 per cent. forge-scale (magnetic oxide of iron) to the glass (preferably a lead glass) to be coloured. The magnetic oxide—which may be replaced by iron filings, tin-foil, &c.—acts as a reducing agent and causes the formation of cuprous oxide, or, in the event of a more powerful reducing agent having been used, of metallic copper. The red oxide or metal is soluble in the glass at the melting point of the latter, so that on withdrawal from the furnace the glass is colourless or slightly tinted with cupric silicates (*v.i.*). Separation of the dissolved copper does not take place when the glass is rapidly cooled, but when the period of cooling is prolonged by placing the glass in a furnace kept at the point of incipient fusion, separation of an opaque layer of deep red colour takes place. **Aventurin** is a glass of this description containing 3 per cent. and upwards of copper. On account of the opacity of ruby-red glass made in this manner, it is chiefly used for "flashing" colourless glass—that is, applying a layer of the coloured to the colourless material. As a rule, the coloured glass is first taken

on to the blower's pipe and is then dipped into the colourless mixture; the glasses must obviously be of similar composition, so that they may weld well and their dilatation by heat be identical.

Ruby glass is also made with gold as a colouring constituent, the phenomena of dissolution and slow separation of the metal being similar to those observed in the case of copper. The gold is applied by wetting the sand (in the glass raw materials) with a solution of gold chloride, drying and mixing with the rest of the ingredients. The quantity of gold requisite to produce the colour is very small, about 1 part in 10,000 sufficing. Other metals that are capable of dissolving in and separating from glass, are silver and lead, silver giving a yellow colour (*v.i.*), and lead a grey stain on cooling. A bluer shade of red than either of the foregoing is obtained by means of manganese, about 2 per cent. of MnO_2 and 4 per cent. of nitre being added, the latter reagent preventing reduction of the manganese.

Yellow glass is manufactured by the use of ferric oxide, lead antimonite (yielding a turbid glass), metallic silver and alkali sulphides, the latter being made *in situ* by adding sulphur to the charge, if it contain alkali carbonate or charcoal, if it be prepared with alkali sulphate. Uranium glass, made by adding 2 to 3 per cent. of an alkali uranate, has a green-yellow colour and is fluorescent. Selenium glass, now made by adding a selenite or selenate and a reducing agent to glass, has an orange or reddish colour. An orange colour can also be produced by the use of a mixture of ferric oxide and manganese dioxide, the yellow-brown caused by the ferric oxide and the red of the manganese being its components.

Green glass, of somewhat dull and impure tint, is yielded by ferrous oxide; yellow-green shades are obtained when ferric oxide is also present. Better greens are obtained from a mixture of cupric oxide and ferric oxide. Chromium oxide, Cr_2O_3, also gives a green with a yellow tone, and when used in considerable proportion renders the glass opaque; the product being known as **chrome aventurin**.

A mixture of CuO and Cr_2O_3 gives an emerald green used for artificial gems.

Blue Glass.—The chief colouring matter for blue glass is cobalt, about 0·1 per cent. of cobalt oxide sufficing. Cobalt glass is prepared in large quantities as a pigment (**smalt**) (see Vol. II., Chap. XV.). Pale blue glasses may be made with a small proportion of cupric oxide and by the partial oxidation of iron green glass.

Violet glass is made by employing manganese dioxide in considerable quantity, the colour being apparently due to manganic silicate, manganous silicate being colourless.

Black glass is actually glass containing any strongly colouring

oxide, such as that of iron, cobalt or manganese, and so dark-coloured as to appear black. Nickel in the reduced state in glass renders it grey.

Opal Glass.—The general method of preparing opal glass—by which term is meant glass of semi-transparent milky appearance—consists in adding to the glass mixture one of several materials, themselves white and opaque, which do not completely dissolve in the glass mixture. The oldest form of milk or enamel glass is that (usually made with lead glass) containing stannic oxide. More recently cryolite, fluor spar and calcium phosphate have been used. Translucent, as distinct from transparent, glass can also be made by rendering the surface of ordinary glass matt, either by grinding—*e.g.*, with the sand blast—or by etching with gaseous hydrofluoric acid, or by dipping in the same acid containing an alkali fluoride. Dilute hydrofluoric acid alone etches glass, but leaves it transparent. The effect of fluoride in giving a matt surface is due to the formation of an alkali silicofluoride which is deposited in fine crystals on the glass. Coloured designs are produced by etching or grinding flashed glass.

Painting on glass is executed by applying the metallic oxide capable of yielding the required colour, mixed with strass, to the surface to be decorated, and firing in a muffle at a temperature sufficient to fuse the easily-melted strass and not the body of the article.

Colouring porcelain is a similar process, the colours being mixed with fusible glazes and applied above or below the glaze proper (see *Porcelain*, Vol. II., p. 148).

Besides the compounds used to produce coloured glasses, pigments for porcelain include iridium oxide, platinum and uranium oxide for blacks, stannic chromate for pink, barium chromate and lead chromate for opaque yellows. Gilding is practised by applying precipitated gold, burning on and burnishing.

Special kinds of Glass.—Borate glasses containing B_2O_3, partly replacing SiO_2, are made for optical purposes. P_2O_5 is a similar substitute for SiO_2; BaO and ZnO may replace CaO, and Tl_2O may be used instead of alkali. The chief merit of glasses of this description consists in the high refractive indices which they possess. Glasses designed to avoid the alteration of the zero point of thermometers made from them are characterised by containing ZnO and B_2O_3. Thus the following is a typical glass of this kind—SiO_2, 52 per cent.; K_2O, 9 per cent.; ZnO, 30 per cent.; B_2O_3, 9 per cent.

Properties of Glass.—The specific gravity varies from 2·4 to 2·6 for alkali-lime glass and 3 to 3·8 for lead glass. Thallium glass is the heaviest known, having a specific gravity of 5·6. The index of refraction of glass decreases as its content of silica

increases, and in general increases with increasing content of the lead oxide or other oxide capable of replacing lead oxide. Although all ordinary glasses appear to be unaffected by water, acids (except HF) and alkalies, when regarded from the standpoint of daily domestic use, yet they are slightly but distinctly attacked by most solutions, and display considerable instability and solubility in the laboratory. In general, glasses with a high content of silica are less easily attacked than those containing a considerable proportion of alkali—this being in accordance with the fact that acid silicates are commonly more refractory than those of more basic character. In laboratory practice it has been found that glass vessels are rendered more resistant to the attack of reagents by exposure to steam for a short time.

CHAPTER VIII.

SUGAR AND STARCH.

SUGAR.—The term sugar is used in two senses. In every-day life it means, when employed without epithet, sucrose or "cane sugar"; by the chemist it is used generically for a certain class of carbohydrates. Adopting for the moment the more extended significance, the following sugars may be cited as of technical importance:—

(A.) Sucroses of the general formula $C_{12}H_{22}O_{11}$.
  (1) Sucrose or cane sugar.
  (2) Lactose or milk sugar.
  (3) Maltose.

(B.) Glucoses of the general formula $C_6H_{12}O_6$.
  (1) Dextrose or grape sugar.
  (2) Lævulose or fruit sugar.*

These two groups are related, in that the members of the first, on hydrolysis, become converted into those of the second, thus—

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

Of these two members of the second group, one is always dextrose, while the other varies with the sucrose from which it has been obtained—*e.g.*, cane sugar on hydrolysis yields dextrose and lævulose, lactose gives dextrose and galactose, and maltose forms dextrose.

(A.) **SUCROSES.**—1. **Sucrose or Cane Sugar, $C_{12}H_{22}O_{11}$.**—This substance—"sugar" in ordinary phraseology—is technically the most important member of the sugar group. Although many other carbohydrates are sweet, the intensity of their flavour falls short of that of sucrose.† This fact has naturally led to the cultivation of plants producing sucrose rather than other sugars, in all cases where the product is required as a sweet food. The name "cane sugar" has become usual on account of the fact that, until about a hundred years ago, sugar was prepared almost exclusively from the sugar cane (*Saccharum*

* The nomenclature of the sugars is in a state of flux, and consequently the older and more familiar names have been adopted here. In modern phraseology, according to one system, the sugars of the general formula $C_6H_{12}O_6$ are termed saccharides, whilst those of the general formula $C_{12}H_{22}O_{11}$ are disaccharides.

† Lævulose is a possible exception.

officinarum). At the present time the term has lost its appropriateness, as more than half the world's production of sugar is now obtained from the beet (*Beta vulgaris*). The sugar from these sources, when perfectly refined, is identical in all respects, though characteristic impurities differentiate the raw sugars and the lower grades of refined products (*v.i.*).

Cane Sugar.—The sugar cane is grown in tropical and subtropical countries, the chief sources of supply being the West Indies, Brazil, Mauritius, Java, the Philippines, Sandwich Islands and Queensland. The cane grows to a height of 8 to 20 feet, the stems being 1½ to 2½ inches in diameter. When ripe it contains about 90 per cent. of its weight of juice, the juice itself containing 12 to 20 per cent. of sugar. The following analysis will serve as an example of a juice of good quality:—

Crystallisable sugar, ...	19·64	per cent.
Uncrystallisable sugar, ...	0·30	,,
Ash, ...	0·25	,,
Water, ...	79·44	,,
Organic matter other than sugar, . . .	0·37	,,
	100·00	,,

After cutting, the canes are worked up for sugar as quickly as possible, for delay means loss of sugar by decomposition. In the older methods of working, which are still largely used, the cane is crushed between rollers, and the juice collected; the residue, termed bagasse, is used as fuel; waste is thus occasioned, as this residue generally retains a notable amount (4 to 5 per cent.) of sugar. The juice, after filtration, is treated with lime (0·15 per cent.) to neutralise any acidity which may have developed,* and is also usually treated with SO_2, these additions serving to hinder fermentation and consequent loss of sugar. It is then heated to 170° to 180° F. = 77° to 82° C., whereby coagulation of the impurities takes place, part appearing as scum, which is skimmed off, and part depositing in the heating vessel.

Concentration.—The clarified juice is then run into evaporating pans set in series over the flue of a furnace. Evaporation is conducted systematically, the weak juice entering the pan furthest from the fire, and being ladled from pan to pan until it reaches that nearest the fire, by which time it has arrived at its point of crystallisation. The size of the pans is graduated (the smallest being at the fire end of the flue), so that their content is appropriate to the volume of liquid to be evaporated. The sugar having been brought to this point of concentration is separated from the portion of the juice which still remains liquid, either by drainage in perforated casks, or by means of a centrifugal machine or hydro-extractor, such as is shown in Fig. 30.

* Any excess of lime combines with the sugar to form a "saccharate."

The former method of separation takes weeks to accomplish. The juice thus separated is either evaporated again and a second crop of crystallised sugar obtained, or it is fermented for the preparation of rum. A good deal of juice of this character containing sugar, which is uncrystallisable from the simultaneous presence of various impurities, is used for food under the name of *treacle* or *molasses*. The nature of this product may be gathered from the following analysis :—

Water, ...	25·87 per cent.
Sucrose, ...	41·91 ,,
Invert sugar,*	25·50 ,,
Ash, ...	3·75 ,,
Organic matter (other than sugar), .	2·97 ,,
	100·00 ,,

It is evident that several improvements in the economy of the process described above are possible. The following have been

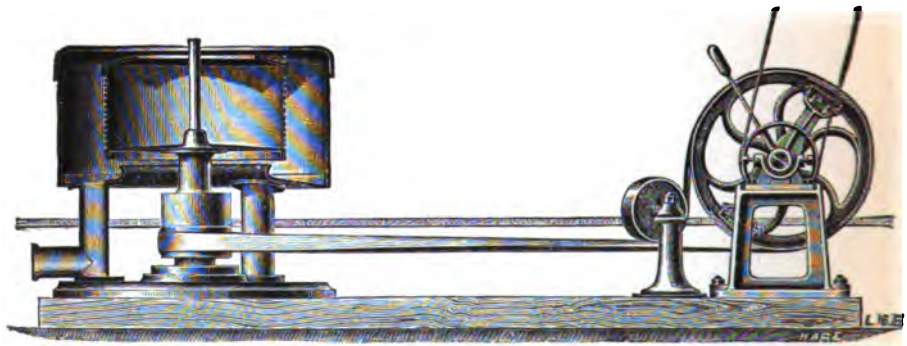


Fig. 30.—Hydro-extractor.

adopted :—(1) The cost of evaporation has been diminished by the use of vacuum pans (see p. 171), and by adopting evaporators of the Wetzel type, in which a revolving frame-work of steam-pipes dips into a trough of the juice to be evaporated and becomes covered with a film of liquid, which is evaporated to dryness as the frame-work performs that part of its revolution which takes place in air (see *Concentration of glycerin*, Vol. II., Chap. XI.). (2) Centrifugal separators are used instead of the method of draining in perforated casks described above, and thus a considerable saving of time is effected. (3) A more radical alteration consists in substituting a process of diffusion for that of crushing, for winning the juice

* The name given to the mixture of dextrose and lævulose obtained by "inverting" sucrose (p. 188).

from the cane. This process is similar to that in general use for the extraction of beet sugar (*q.v.*), and gives an output which is stated to be about 15 per cent. higher (reckoned on the total sugar in the cane) than that obtained by the older method of crushing between rolls. The stouter cell walls of the cane prevent this process being as effective as it is for beet.

The quality of raw cane sugar varies largely on account of the different methods of extraction, clarification and evaporation adopted, but a typical sample will contain about 89 per cent. of sucrose, 4 per cent. of glucose, 4 per cent. of moisture, 1·5 per cent. of ash, the balance being various organic impurities. The method of refining is described below, after the extraction of sugar from sources other than the sugar-cane has been dealt with.

Beet Sugar.—The plant used is a variety of the common beet, improved by careful cultivation. The cells in the parenchyma of the beet are narrow close tubes, having the usual layer of protoplasm adhering to the cell-wall, and containing the cell-sap which is present in such abundance that it constitutes about 96 per cent. of the weight of the root. The sap contains 20 per cent. of solid matter in solution, the chief constituent of this being sucrose, together with a little **raffinose**, $C_{18}H_{32}O_{16}.5H_2O$. Minor substances present are albuminous and colouring matters, asparagine, betaine, $CH_2[N(CH_3)_2]CO_2CH_3$—which collects in the residues from the sugar and is used as a source of trimethylamine —glutamine, pectinous substances, coniferine—which yields vanillin during the treatment of the beet juice—and various organic acids (tartaric, malic, &c.), as well as the usual mineral constituents of plants.

Extraction.—In manufacturing sugar from beet, the roots are freed from dirt, rasped, and the resulting pulp placed in woollen bags, and the juice squeezed out by an hydraulic press, the yield being about 77 per cent. of juice as compared with 96 per cent., the amount contained in the roots. On account of the cost of cartage, the beets grown in outlying fields are frequently crushed between rollers on the spot, and the juice, after treatment with about 1 per cent. of lime, is conveyed by pipe-lines to the central factory where it is worked up. This method of extraction is in use in France, but in Germany has been almost entirely displaced by the **diffusion process.** In this process the beet is shredded into small thin strips so as to expose an ample surface to the water with which it is subsequently extracted ; these strips or **cossettes** (which are about $\frac{1}{4}$ inch in breadth and $\frac{1}{30}$ inch in thickness) are brought into contact with water, and the sugar in the beet-sap diffuses out through the cell walls while colloid substances remain in the cells. Thus, at a single operation, a juice is obtained which is less impure than that procured by any process of expression in which the cell walls are crushed and broken.

It might be thought that the diffusion process would yield a bulky diffusate, the evaporation of which for the recovery of the sugar would be a costly operation; but this is not the case, as the diffusion is carried on systematically, and thus the quantity of water needed is reduced to a reasonable limit. Several forms of apparatus for systematic extraction are used in the diffusion process, typical examples of which will be described. A common form of diffuser consists of a "battery" of cells connected together so that water can be caused to travel from one to the other through the series. The sliced beet is filled into the cells and the water circulated, traversing in its passage between each pair of cells a tubular heater, in which it is warmed to a temperature ranging from 20° to 90° C. = 68° to 194° F. It is usual to graduate the temperature in the heaters between the cells, it being gradually raised from the lower to the upper limit quoted above in passing through the series of cells. A high temperature favours the rapidity of diffusion, but impairs the quality of the juice to some extent. When the apparatus is in regular operation the fresh water comes into contact with nearly exhausted beet, while the nearly saturated water is used to extract fresh beet with its full complement of sugar. Of the whole series of cells—commonly 10 to 12 in number—one, containing the extracted beet, is being emptied, while another is being filled with fresh beet, and the remainder present a regular gradation of extraction. The quantity of water above that contained in the sap of the beet itself is thus kept comparatively small, and nevertheless repeated treatment with wash water of decreasing content of soluble matter is secured. The cells are generally arranged in a circle for convenience of working, and a radial spout delivers the sliced beet from a central hopper into any desired cell.

A second form of diffuser may be mentioned as it is an obvious extension of the idea underlying the apparatus described above. It consists of two concentric cylinders with a screw-shaped guide in the annular space between them. The inner cylinder rotates and forces the sliced beet along the screw in the annular space, causing it to meet a current of water into which the juice diffuses. The fresh water meets the exhausted beet, and the water rich in sugar (and thus largely deprived of its extractive power) makes its exit from the end at which the fresh beet enters, both systematic extraction and continuous working being secured. The temperature of the liquid can be regulated by the use of steam coils.

Whichever process of diffusion is used, a good degree of exhaustion is obtained; the spent beet containing little or no sugar, but sufficient nutriment to make it available as fodder. It is, of course, very wet, about 92 per cent. of its weight consisting of water, and is generally pressed and, preferably, dried before

it is utilised as food. Its nutritive value is indicated by the following analysis of the dry material :—

Water,	5·34 per cent.
Albumin,	7·34 ,,
Proteids (as distinct from albumin),	1·04 ,,
Fat,	0·90 ,,
Starch,	56·62 ,,
Non-nitrogenous extractive matter,	2·65 ,,
Crude fibre,	20·67 ,,
True ash,	5·10 ,,
Sand,	0·34 ,,
	100·00 ,,

The crude juice is fairly free from suspended matter, but is nevertheless strained through sieves before defecation. As in the case of juice from the sugar cane, it is necessary to purify beet juice before concentration by treatment with lime, which neutralises any acid substances which might invert (p. 188) the sucrose in the juice. In modern practice, enough lime—viz., about 3 per cent. of the weight of the beets from which the juice has been obtained—to convert the whole of the sucrose into calcium monosaccharate ($C_{12}H_{22}O_{11}CaO,H_2O$) is added, and the saccharate is decomposed immediately it is formed by treatment with CO_2, which is blown into the vessel in which the defecation with lime is effected. It appears that the comparatively bulky precipitate of calcium carbonate which is thus formed carries down with it much of the colouring matter and various impurities, yielding a better juice than that obtained by employing a smaller quantity of lime, such as would suffice for neutralising the organic acids naturally present in the juice. The process is carried out in a covered tank heated by close steam (to avoid dilution of the juice) and provided with a perforated delivery tube through which CO_2 can be blown in. The order of operations consists in the admission of the juice to be defecated, the addition of lime either as milk of lime or unslaked in small lumps, and heating and carbonating the resulting mixture. Excess of CO_2 must be avoided, as carbonic acid is capable of causing a certain amount of inversion (p. 188). The gas is, therefore, admitted until the alkalinity of the juice corresponds with the presence of about 0·1 per cent. of lime. To complete the defecation, the juice after filtration from the sludge (which consists chiefly of calcium carbonate) is re-treated with a smaller quantity—*e.g.*, 0·5 per cent.—of lime, and the carbonation repeated ; a liquid approximately neutral is thus obtained. The neutralisation of the lime by CO_2 is necessary, inasmuch as it would otherwise, on boiling, react with the albuminous substances contained in the crude juice, and yield soluble decomposition products instead of forming a precipitate and freeing the juice from impurities of the albuminous class.

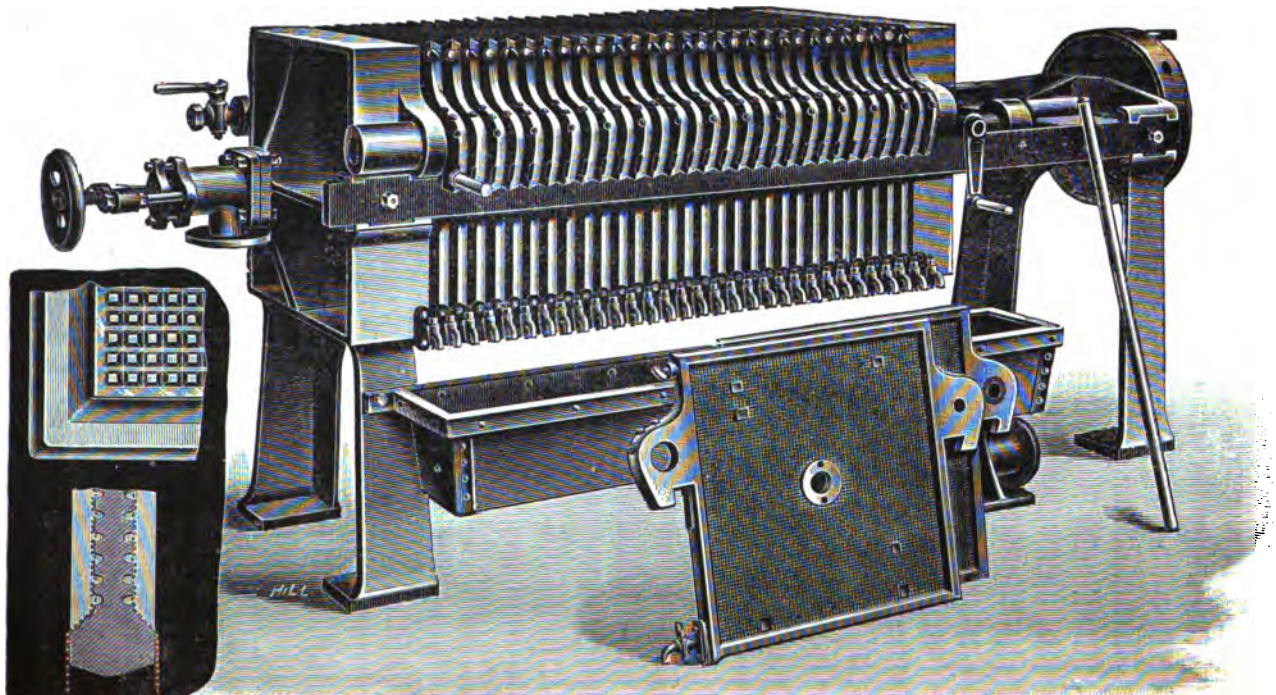


Fig. 31.—Filter press, as made by Messrs. S. H. Johnston & Co., of Stratford, E.

The CO_2 is usually obtained in the form of lime-kiln gases, produced either in ordinary kilns or in those of the Dietzsch type (see *Lime and Cement*, Vol. II., p. 135). The kilns are provided with collecting flues, through which the gas is drawn off; it is then scrubbed and freed from SO_2* and dust. Where the residues from the refining process (molasses) (*v.i.*) are fermented for spirit manufacture, another source of CO_2 is available (see *Brewing and Distilling*, Vol. II., p. 199), but no application of this fact appears to have been made on a manufacturing scale. Seeing that lime is needed in any case, CO_2 as a bye-product is inevitable.

The final removal of the sludge formed during the lime purification is effected in filter presses of such construction (Fig. 31) that the sludge can be washed and adhering sugar recovered. By this means the content of sugar is reduced to 2 to 3 per cent. of the weight of the dried sludge, which amounts to about 10 per cent. of the beets treated. The sludge is composed of about 75 per cent. of calcium carbonate, the balance consisting of the calcium salts of the organic acids of the juice, small quantities of magnesia and alkalies, and a certain amount of insoluble organic matter. As it contains on an average 1 to 2 per cent. of P_2O_5, 0·3 to 0·5 per cent. N, and 0·2 to 0·3 per cent. K, it finds a use as a manure. When purification in this manner is carefully conducted, the juice is not necessarily decolorised by animal charcoal, but in general the use of this material is found requisite. The method of treatment is similar to that practised in the purification of the refined juice after concentration (*v.i.*). An alternative plan at this stage consists in treatment with sulphur dioxide and filtration through sand, which eliminates residual lime as calcium sulphite, and also decolorises the liquid. The SO_2 is usually applied by blowing the products of combustion from a small kiln burning sulphur into the juice, care being taken that the point of neutrality is not overstepped. The antiseptic properties of the small quantity of sulphite remaining in solution are useful in preventing fermentation of the purified juice. Phosphoric acid has been suggested as a precipitant for residual lime, on the ground that it causes a better removal of the organic matter (other than sugar) than can be effected by CO_2. The sludge containing calcium phosphate has a manurial value corresponding with that of the phosphoric acid used.

Concentration.—The juice purified by the methods given above, is somewhat dilute from the addition to it of the washings of the sludge separated by the filter press, and has a specific gravity of about 6° Beaumé—*i.e.*, 1·043†—corresponding with a

* This gas is removed, not on account of its being objectionable as far as the sugar is concerned, but because it attacks the fittings of the pumps used to draw it from the kilns.

† The strength of sugar solution is sometimes stated in "degrees Brix," which are designed to represent the percentage of sugar directly; thus, juice of 10° Brix contains 10 per cent. of sugar.

content of about 11 per cent. of sugar. It is concentrated in "multiple effect" evaporators, the principle of which consists in the use of the steam from one pan, boiling under a pressure somewhat less than that of the atmosphere, to heat the liquid in the next pan, boiling under a still smaller pressure. A series of three such vessels (**triple effect**), the contents of which boil under continually diminished pressure, is usually found the most efficient arrangement, doubtful economy being obtained on extending the system to four or more pans. An apparatus of recent design, which has found considerable application in sugar concentration, is the Yaryan evaporator, the essential parts of which are shown in Fig. 32. The juice to be concentrated flows from the pipe, A, through a series of horizontal tubes, B, set in

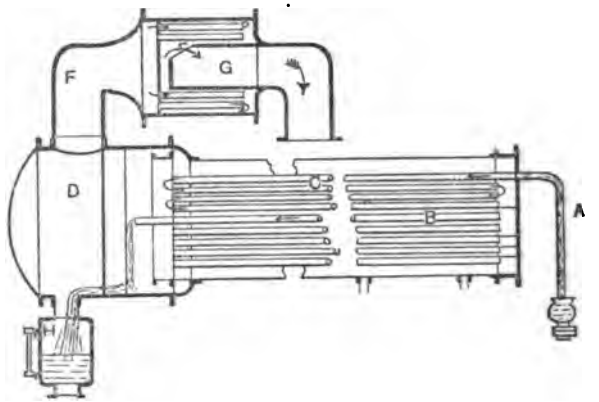


Fig. 32.—Multiple effect evaporator.

A, Inlet pipe; B, tubes; C, cylinder; D, drum; H, chamber; F, pipe for exhaust steam; G, box for catching spray.

a cylinder, C, serving as a steam jacket. During its passage through these tubes, its temperature is raised by the heat transmitted from the steam through the walls of the tubes, and it boils under the diminished pressure, which is maintained by an ordinary exhaust pump. The steam and liquid emerge into a short, wide drum, D, at one end of the heating cylinder, and the steam is drawn off by the pump through the pipe, F, while the liquid collects in the chamber, H. Any liquid carried over as spray by the steam on account of the tumultuous boiling of the juice, is caught in the box, G, in which the steam is compelled to take a circuitous course, and to pass through narrow tubes and passages, and thus to deposit any suspended matter which it may contain. The liquid separated in this manner is returned to H. The exhaust steam from G serves to heat the

liquid in the tubes of the next evaporator, the exhaust steam from which in turn heats the third member of the series. The diminution of pressure is progressive, as mentioned above; the pressure in the last evaporator being as low as can be obtained in practice. The advantage of this arrangement is that the juice is never heated to its boiling point under atmospheric pressure, and thus loss of sugar by inversion (p. 188) is largely decreased. The economy of heating also obtained is considerable, a matter

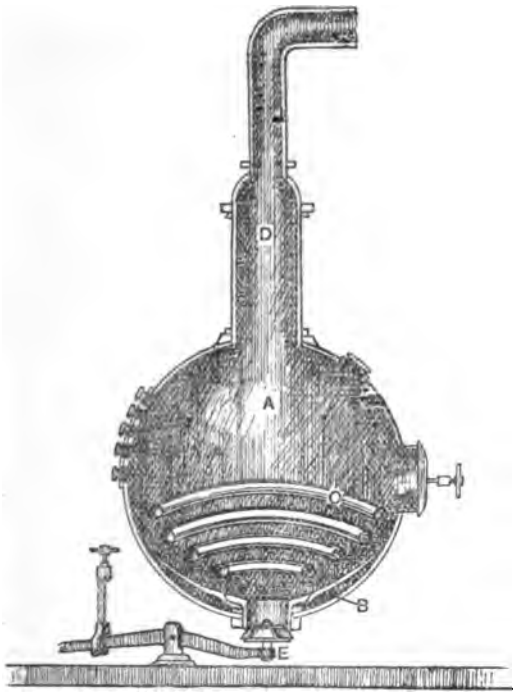


Fig. 33—Vacuum pan.

A, Vacuum pan; B, double bottom; C, steam coil; D, head; E, valve.

of moment, seeing that the quantity of water to be removed is very large. A short boiling at atmospheric pressure of the concentrated juice before the crystallisation of the sugar therefrom, is found necessary in order to complete the clarification, the low temperature of the triple effect apparatus not sufficing to coagulate the whole of the impurities removable at this stage. The juice is brought by this process to a concentration of 20° to 30° Beaumé (specific gravity 1·16 to 1·263), and contains 35 to 55 per cent. of sugar. Any residual lime is removed

by addition of sulphurous acid or phosphoric acid, and the juice is filtered either in a filter press or through animal charcoal. Concentration is then continued in a vacuum pan. The older form of this apparatus consists of a globular copper vessel, A (Fig. 33), with a double bottom, B, and a steam coil, C, for heating its contents. The upper part of the vessel is fitted with a head like a still, D, connected with an exhaust pump, by which means a vacuum is produced and maintained in the pan. The juice, when sufficiently concentrated, is drawn off through the valve, E. Cylindrical iron vacuum pans are also used in modern practice. In working the vacuum pan, the concentrated juice (previously warmed) is run in, and steam at 50 to 60 lbs. pressure is admitted to the double bottom and coil. The exhaust pump reduces the boiling point of the concentrated juice to 60° to 80° C. = 140° to 176° F., and evaporation proceeds until the contents of the pan has reached a concentration such that it contains 70 to 90 per cent. of sugar. The product is termed **massecuite**. A juice with but little impurity yields a mass of sugar crystals (mixed with syrup) at this stage, the crystals being fine if the concentration has been rapidly executed, and coarse if the contrary condition has obtained. An impure juice gives a syrup from which crystals are deposited only after standing for some time. The satisfactory conduct of the concentration requires much personal skill and experience. It has lately been pointed out that the use of moderately high pressure steam (50 lbs.) is not advantageous, as local overheating of the massecuite may occur. Steam of low pressure (of course in correspondingly larger amount, involving the use of larger heating surfaces) is distinctly preferable. The massecuite is separated in a centrifugal machine, the crop of crystals being termed **first jet** sugar. Two succeeding crops of inferior quality (**second** and **third jet**) can be obtained by boiling down the mother liquor, the final residue of which constitutes beet molasses; methods of utilising this material are described below. About 70 per cent. of the sugar in the beet is obtained crystallised as raw sugar of one or other of these grades.

Utilisation of Uncrystallised Sugar. — The difference between the quantity of sugar contained in the beet and that obtained as raw sugar, in a saleable condition, by the processes described above, amounts to about 30 per cent. of the whole. Of this about one-half (15 per cent.) is lost in the course of manufacture, and the remaining 15 per cent. is left in the molasses separated from the sugar crystals by treatment of the boiled-down purified juice in a centrifugal machine. The crystallisation of this residual sugar is rendered impracticable by the presence of organic substances, other than sugar and of mineral matter. The raffinose (p. 165) present in

the beet also becomes concentrated in the molasses. At one time this residue was chiefly utilised for the manufacture of spirit, it being unfit for food on account of its nauseous flavour. As already stated, cane-sugar molasses is edible. According to modern practice, beet molasses is usually worked up for crystallisable sugar, by one or other of the processes about to be described. Choice between utilisation for sugar or spirit making depends largely on the fiscal regulations of the country in which the manufactory is situated, this part of the manufacture being —as indeed is the whole industry—hedged about by privileges and restrictions purely arbitrary in character. The method of preparing spirit from molasses differs in no essential respect from the processes of fermentation and distillation applied to other saccharine materials (see *Brewing and Distilling*, Vol. II., p. 189), and needs no further comment. The recovery of crystallisable sugar, however, is effected by methods of comparative complexity. An average sample of beet molasses has the following composition :—

	Per cent.
Sugar,	50·0
Organic matter (other than sugar),	20·0*
Potash,	5·5
Mineral matter (other than potash),	4·5
Water,	20·0
	100·0

(1) **The Osmose Process.**—This depends upon the fact that when molasses is separated from water by an osmotic membrane—*e.g.*, parchment paper—the salts in the molasses diffuse more quickly than the sugar into the water; a portion of the sugar left in solution can be recovered on evaporation. Some dilution from the incoming water takes place under these conditions, but the process has the advantage of simplicity and of requiring no addition, other than water, to the molasses to be treated. The organic matter (other than sugar) present in the molasses diffuses even more slowly than the sugar, and remains in the liquor sent for concentration; its presence hinders the separation of the whole of the sugar, and necessitates the return of the molasses produced by concentration and subsequent centrifugal separation, to the osmose apparatus. Three osmotic treatments of the same portion of molasses are as many as can be profitably performed, about half the total sugar in the molasses being thus recovered. The process is carried out in an apparatus somewhat resembling a filter press in structure, consisting of a series of compartments separated by septa of parchment paper (see *Paper and Pasteboard*, Vol. II., Chapter XIV.). The molasses is fed into alternate compartments, and the water into the intermediate divisions.

* Containing 1·9 per cent. of nitrogen.

The weak saline solution obtained by the passage of the water through the second series of compartments is usually too dilute for use save as liquid manure. In France and Belgium, where beets yielding much nitrate are grown, the water from the osmose process is sometimes worked up for potassium nitrate. The residual molasses, though poorer in mineral salts, is richer in colloidal organic matter than is the original molasses, and generally goes finally to the distillery.

(2) **Processes depending on the Formation of Compounds of Sugar with the Alkaline Earths.**—The property possessed by sucrose of forming loose compounds—saccharates or sucrates—with lime, strontia, and baryta is turned to account in various processes for the recovery of crystallisable sugar from beet molasses. The following are typical methods of this class:—

(*a*) **The Elution Process.**—The molasses is mixed by means of an edge-runner with about 25 per cent. of its weight of quicklime, but little reaction taking place as long as the mixture is kept cool; on this account the pan of the edge runner is artificially cooled. When incorporation is complete, the mass is transferred to small iron chambers, in which its temperature rises spontaneously to 100° C. = 212° F. or higher, and combination of the sugar with the lime to form tricalcium saccharate ($3CaO, C_{12}H_{22}O_{11}, 3H_2O$) takes place, accompanied by expulsion of the surplus water and the formation of a hard porous mass. This product is broken up and extracted systematically with weak alcohol (35 per cent.), impurities being dissolved and the calcium saccharate left fairly free from foreign matter. The extraction is carried out in an apparatus resembling a battery of diffusion cells (p. 166). The alcoholic extract is distilled and the alcohol recovered, the aqueous residue being used as a manure. The alcohol left clinging to the calcium saccharate is removed by steaming and is also recovered. During the steaming the tricalcium saccharate is partly decomposed, yielding monocalcium saccharate, $C_{12}H_{22}O_{11}CaO,H_2O$, and lime. The complete separation of the lime can be effected by treatment with CO_2, but the monocalcium saccharate is often substituted for lime, in the early stages of the winning of raw sugar, for neutralising the acidity of the diffusion juice (p. 167); the acid thus neutralised of course liberates an equivalent quantity of sugar which is worked up with the bulk. Various modifications of the elution process have been devised, differing chiefly in the manner in which the calcium saccharate is produced, but their underlying principle is identical with that enunciated above. **Staffen's process** is distinguished from its congeners by the fact that the use of alcohol is dispensed with. The molasses is diluted with water until its content of sugar is about 7 per cent., and to it quicklime is added in small portions, the total quantity being about equal to the weight of sugar present. The liquor is well stirred during admixture to prevent the temperature

rising above 15° C. = 59° F. At first the lime goes into solution, but eventually it separates again as tricalcium saccharate accompanied by excess of lime. The mass thus obtained is filter-pressed, and the saccharate used instead of lime in purifying the crude juice (p. 167). The expressed liquid is utilised as manure and the washings are used for diluting the next batch of molasses.

(*b*) **Strontia Processes.**—Several processes have been devised, notably by Scheibler, in which strontia is substituted for lime in recovering sugar from beet molasses. The earlier of the processes due to this chemist consists in treating the molasses with strontium hydroxide in sufficient proportion to form distrontium saccharate, $2SrO.C_{12}H_{22}O_{11}$, and to leave an excess of strontium hydroxide, in a solution of which the saccharate is almost insoluble. The precipitate is thrown on a filtering cloth stretched over a horizontal semi-cylindrical vessel. The air beneath the filtering cloth (which is, of course, supported by a perforated plate) is exhausted, and the de-sugared liquid pulled through. The distrontium saccharate is washed with a hot solution of strontium hydroxide, turned out into iron boxes by inverting the filter, and treated with water at a temperature below 15° C. = 59° F.; cold-air chambers are requisite in warm weather for this part of the process. The saccharate is decomposed, giving crystals of strontium hydroxide and a solution of sugar, which is freed from residual strontia by treatment with CO_2, and concentrated in a vacuum pan in the usual way. That part of the strontium hydroxide which crystallises is immediately available for further use, while that precipitated as carbonate is causticised by burning in a special kiln (*v.i.*). A more recent modification by Scheibler depends on the formation of monostrontium saccharate, $SrO.C_{12}H_{22}O_{11}$, when a solution containing about 25 per cent. of sugar is treated with strontium hydroxide at about 70° C. = 158° F. A slight excess of strontium hydroxide is used, and the temperature is maintained above that at which the formation of distrontium saccharate takes place. The instability of mono-strontium saccharate is such that the addition of a crystal of strontium hydroxide determines the precipitation of the same hydroxide, and that of a crystal of monostrontium saccharate causes the same salt to be thrown down. To the liquid is, therefore, first added a crystal of monostrontium saccharate, and the precipitate filtered off; the filtrate is boiled with strontium hydroxide, yielding distrontium saccharate as a precipitate, which is used instead of strontium hydroxide for treating a further portion of molasses, another crop of monostrontium saccharate being thus obtained. The total yield of monostrontium saccharate is decomposed by dissolution in water, thorough cooling, and the addition of a crystal of strontium hydroxide. The recovered strontium hydroxide can be used again in the process; the sugar is freed from remaining strontia

by means of CO_2. The filtrate from the distrontium saccharate obtained above yields on crystallisation crude strontium hydroxide; residual strontia is recovered as carbonate, and the final filtrate contains the impurities of the molasses; it is worked up for potash or used as manure.

The strontium hydroxide used in this process is generally prepared in the sugar factory by burning native strontium carbonate (*strontianite*) to caustic strontia, much in the same way as limestone or chalk is burnt to caustic lime.* A gas furnace is preferable for this purpose, as the comparatively costly strontia is thus not contaminated with the siliceous ash of solid fuel, and for a like reason the furnace should be basic-lined (see Vol. I., p. 8). Strontia being a more powerful base than is lime, has a stronger tendency to act upon acid materials (*e.g.*, siliceous bricks) and also requires a higher temperature for the decomposition of its carbonate. The strontium carbonate obtained as a bye-product in the process for winning crystallisable sugar from molasses, is taken from the filter press, moulded into bricks, and burnt in the same manner as the native carbonate. The caustic strontia is hydrated and dissolved in water, the hot solution, containing about 13 per cent. of SrO, being run off and allowed to crystallise, nearly the whole of the strontia being deposited in the hydrated state as $Sr(OH)_2.8H_2O$.

The saccharates formed by the use of baryta instead of strontia have also been used for the separation of sugar from molasses, but the processes thus devised are essentially similar in principle to those depending on the formation of the corresponding strontia compounds.

(3) **Processes depending on the Direct Removal of Potash.**—Several processes of this type have been devised, but only one has been practised on any considerable scale. The alum process of Duncan and Newlands consists in heating the molasses with a strong solution of aluminium sulphate, in such quantity as suffices to form alum with the potash salts present. The alum is separated, the liquid treated with lime, heated to 160° F. = 71° C., and filtered, the filtrate containing sugar in a crystallisable condition. The value of the alum obtained as a bye-product is said to cover the cost of the aluminium sulphate used.

Another method of utilising beet molasses consists in fermenting and distilling (as mentioned above), and working up the residues after charring (*Schlempekohle*) for potash (see *Minor Chemical Industries*, Vol. II., Chap. XVIII.).

Minor Sources of Sugar.—Although by far the major part of the sugar consumed by civilised nations is obtained from the

* *Cœlestine* (native strontium sulphate) is also used as a source of strontia.

sugar cane or the beet, yet there exist several minor sources of supply that have a certain local importance. The trade in these classes of sugar is so inconsiderable that the preparation is conducted in a crude and simple manner, involving the application of no chemical principle other than those already included in the description of the chief sources of sugar.

Maple Sugar.—This is obtained from the juice which flows from incisions in the sugar maple (*Acer saccharinum*). The juice is merely boiled down until it solidifies, forming a crude sugar, consumed in rural districts in the United States and in Canada.

Palm sugar is won in a similar manner from the juice of the date palm (*Phœnix sylvestris*) and trees of like species.

Sorghum Sugar.—Extensive experiments have been made in the United States on the cultivation of *Sorghum saccharatum*, which is a graminaceous plant, the juice of which contains sugar (5 to 10 per cent.). Hitherto the results have been of little industrial value on account of the fluctuation of the content of sugar, and the presence of non-saccharine constituents in the juice which hinder the crystallisation of the sugar.

Refining Raw Sugar.—A good deal of raw cane sugar—*i.e.*, sugar obtained by simple separation by draining, or by means of a centrifugal machine, from the product of the concentration of the purified juice—is consumed as "moist sugar" (Demerara), though much that is sold under this title is merely one of the lower-grade products of the refining process. Raw beet sugar is not fit for food on account of the objectionable flavour possessed by its impurities. The process of refining is essentially the same for sugar of all sources, although, of course, a raw sugar of fair purity is treated more easily than one containing much foreign matter. Sugar, when completely refined, as in the case of loaf sugar of good quality, is almost pure sucrose, and is of identical flavour and sweetening power whatever its origin. The superstition that refined beet sugar is inferior in sweetness to cane sugar has arisen from the fact that formerly, when beet sugar was less completely refined than it is at present, its sweetness was diminished and its flavour impaired by the small quantity of alkali salts which it contained. Repeated tests have shown that it is impossible to distinguish the source of refined sugar by taste.

Raw sugar varies considerably in composition, but a common content of sucrose is 90 to 95 per cent., the balance consisting of water, mineral constituents, organic matter other than sugar, and a little invert sugar. The system of refining generally practised is carried out in the following stages:—

Dissolution.—The raw sugar is dissolved in water by the aid of open or close steam, a solution containing about 50 per cent. of sugar and having a temperature of about 70° C. = 158° F. being obtained. When very crude sugars are refined, defecation by

the addition of blood, and heating until coagulation of the albuminous matter thus introduced occurs, is sometimes necessary.

Filtration.—The solution, if of beet sugar, may sometimes be filtered in a filter press, but if of cane sugar, usually needs a different method of treatment. In this case it is filtered through bags of a cotton fabric ("twill"), arranged in an apparatus known as a Taylor filter. This consists of a cast-iron box covered with a perforated plate, from which depend long, narrow bags of hemp. Inside each bag is the filter bag proper, of twill, as stated above. The mouth of each twill bag is tied on to a nozzle set in one of the perforations of the plate covering the cast-iron chamber. This plate forms the bottom of a shallow tank resting on the chamber, and serving to distribute the sugar solution to the whole of the bags. By means of the large filtering surface exposed by the bags, filtration proceeds at a fair rate in spite of the slimy character of the suspended matter in the sugar solution. The bags after use are either washed *in situ*, or turned inside out and washed in tanks. In the former case, the weak liquor is used at once for dissolving a fresh batch of sugar, while in the latter case the turbid liquor is defecated with lime, filtered in a press, and then used for the same purpose.

Decolorisation.—This is effected by means of animal charcoal (*q.v.*). The charcoal is packed in large iron towers, provided with a perforated false bottom and a filtering cloth. The clear, warm sugar solution is run on to the charcoal at the top, and the air expelled at the bottom until the tower is full, when it is allowed to stand for some hours. The clear, decolorised liquid is then drawn off at the bottom of the tower, while fresh liquor is run on at the top, the operation being continued until the liquid ceases to be satisfactorily decolorised. When the yellow colour of the liquor shows that the decolorising power of the charcoal has been exhausted, the supply of fresh liquor is stopped, and a stream of water is substituted; a good deal of liquor still remaining in the tower is thus expelled without being much diluted by the incoming water, but the remainder ("char water") is comparatively poor in sugar, and has to be returned to the cycle of operations—*e.g.*, used for dissolving the raw sugar. The function of the char (which usually contains about 10 per cent. of impure carbon—having a content of 10 per cent. of its weight of nitrogen—80 per cent. of calcium phosphate, and about 10 per cent. of calcium carbonate) consists in the withdrawal from the sugar solution of many of its impurities, both organic and inorganic; calcium saccharate, which may be present in the liquor, may be decomposed, and the sugar therein set free. The rationale of the action is not well understood. Wood charcoal, although richer in carbon, cannot be substituted for animal charcoal. The fine state of division of the carbon in the latter, spread as it is over nine times its weight of mineral

matter, is probably one cause of its efficacy, but its content of matter other than C, notably N, also appears to be concerned in its decolorising influence. The char after use is "revivified" by washing and reburning. The washing is generally effected by prolonged treatment of the char with boiling water, but sometimes hydrochloric acid is used, in amount calculated to dissolve the lime salts taken up from the sugar solution, while leaving those naturally present in the original char unattacked. The organic matter may be also eliminated by allowing fermentative decomposition to set in, and washing out the products of the changes thus produced. The washing, however performed, is followed by "reburning," the process consisting in heating the char, out of contact with air, to a temperature of about 1,200° F. = 649° C. A pipe kiln is generally adopted for reburning, though revolving cylinders, externally fired, are sometimes used. In the case of the former, the char is fed into the upper ends of cast-iron pipes of elliptical section, set vertically in groups, and heated from below by a furnace. The wet char thus enters at the cooler end of the pipes, is there dried, and is more strongly heated as it descends, finally emerging at the lower and hotter end of the pipes into sheet-iron cooling pipes provided with valves, so that successive portions of the reburnt char can be dropped out and conveyed to the decolorising towers. After repeated reburnings, the char ceases to act efficiently, and is sold as manure.

Evaporation of the Decolorised Liquor.—The liquor is boiled down in a vacuum pan similar to that used in concentrating purified juice for the production of raw sugar. A typical pan of the older spheroidal type has been already shown diagrammatically in Fig. 33. The body of the pan has one or two glazed openings, so that the process of concentration can be watched, and a "proof-stick" or rod for taking samples without opening the pan is also provided. The boiling down is carried on at a temperature ranging from 120° to 190° F. = 49° to 88° C., according to the quality of the sugar to be produced. In general the larger the size of the crystals required, the higher the temperature adopted. The advantages of the use of a vacuum pan have been already mentioned under concentration of purified juice.

The product from the vacuum pan termed **massecuite** is run into a receiver and transferred to a centrifugal machine in which the crystals are freed from adhering syrup. The syrup is worked up for a fresh batch of lower grade sugar, and the final liquid portion, which fails to yield crystallisable sugar, is sold as treacle. The crystals may be sold as such or moulded into cube sugar (*v.i.*). Moist sugar, which is white when separated from the massecuite, is often coloured yellow to imitate genuine moist sugar, such as Demerara. For this fraudulent purpose artificial

dyestuffs are freely used. Even in genuine Demerara, steps are taken to fix the natural colour by the addition of stannous chloride solution to the magma from the vacuum pan; most of the tin is drained away with the molasses, but from $\frac{1}{4}$ to $\frac{1}{3}$ grain of tin per lb. of sugar may remain.

Preparation for the Market.—The refined sugar may be sold as crystals, or in loaves or cubes. Sugar loaves are prepared by running the massecuite into conical moulds, the small end of which is somewhat rounded, departing from the shape of a true cone in order to facilitate the removal of the sugar from the mould. In the smaller end of the mould is a hole closed by a peg. After filling, the moulds are set, each with its small end downwards, and the liquor adhering to the crystals of the massecuite is allowed to drain away. A layer of sugar at the wider end of the mould is removed and made into a magma with a nearly saturated solution of refined sugar, and then poured back into the mould. The loose pulpy mass thus forms a sort of filter bed which aids the even distribution of the solution of sugar caused to percolate from the wide to the narrow end. As the liquor filters through and runs out at the lower end, a fresh portion is poured on to the upper end, the operation being repeated until all the originally adhering liquor of the massecuite is expelled. The sugar loaf is then allowed to drain, removed from the mould, and dried by hot air. Various other methods of making "lump" as distinct from "loaf" sugar are in use. Thus, cubes of sugar may be prepared by filling pure white crystals of sugar, moistened with a little pure solution of sugar, into cubical moulds set in the external surface of a rotating drum, and consolidating the mixture by regulated pressure. The soft moulded cubes are removed automatically and stoved.

Sugar candy is prepared by simply allowing a solution of sugar to crystallise on threads strung in the vessel containing the solution. The white variety is pure sugar; the yellow or brown should be less pure cane sugar, retaining a portion of those constituents which give it the pleasant flavour characteristic of genuine Demerara; refined sugar artificially coloured is, however, often substituted. Well-refined white sugar, from whatever source and of whatever form it may be, contains 99·8 to 99·9 per cent. of sucrose; the balance is chiefly water, only traces of ash and organic matter other than sucrose being present. The faint yellowish tint sometimes retained even by well-refined sugar is hidden by the addition of a small quantity of some blue colouring matter, usually ultramarine. Pure cane sugar has a dextro-rotatory power of $\alpha_D = 66{\cdot}5°$.

2. **Lactose or Milk Sugar,** $C_{12}H_{22}O_{11}.H_2O$.—This may be regarded as a purely pharmaceutical preparation, the manufacture being, of course, insignificant compared with that of sucrose.

Milk contains about 5 per cent. of milk sugar, which can be extracted by the following method:—The bulk of the fat is removed by a separator for butter making, and the "separated" milk heated to from 75° to 85° C. = 167° to 185° F., and treated with 10 per cent. of milk of lime, whereby the residual fat and casein are precipitated. Saturation with CO_2 follows, as in the purification of beetroot juice (*v.s.*), and the purified liquid is concentrated and the milk sugar crystallised. It may be purified by dissolution in water and precipitation by alcohol. Milk sugar is less soluble than cane sugar, requiring about 5 parts of cold water. It is dextro-rotatory, the normal rotation being $\alpha_D = 52{\cdot}5$. A recently-prepared solution exhibits the phenomenon of bi-rotation, or of semi-rotation, according to the method of its formation; on standing or heating, normal numbers are obtained.

3. **Maltose,** $C_{12}H_{22}O_{11}.H_2O$, is prepared commercially in small amount. It is formed by the action of diastase on starch (see *Brewing and Distilling*, Vol. II., p. 197). If required approximately pure, it is separated from the mass obtained by acting upon starch with malt, by extracting with alcohol of specific gravity 0·820, and allowing the solution to crystallise. It is slightly sweet, readily soluble in water, and its solution has a dextro-rotation of 140°.

(B.) **GLUCOSES.**—1. **Dextrose** (*grape sugar*), $C_6H_{12}O_6.H_2O$, occurs in the juice of ripe fruits, accompanied by its isomeride, lævulose, and frequently by sucrose. The quantity varies from 10 to 15 per cent. in grapes to 1 to 4 per cent. in peaches and plums. Dextrose is very soluble in both cold and hot water, in this respect resembling cane sugar. It has about two-fifths the sweetening power of cane sugar. It has a rotatory power of $\alpha_D = 52{\cdot}5$, and exhibits the phenomenon of bi-rotation. On heating to 170° C. = 338° F. it is converted into the anhydride glucosan, $C_6H_{10}O_5$, the taste of which is scarcely sweet. At a higher temperature, 200° to 220° C. = 482° to 518° F., it yields **caramel,** much used as a colouring material for beer and other liquids. Caramel may also be prepared by heating cane sugar. Dextrose was at one time prepared from grapes, but now it is made by the hydrolysis of starch, the product being commercially called starch sugar.

Starch Sugar.—The starch, which is usually that from potatoes or maize, is made into a cream with cold water, and run into boiling dilute sulphuric acid. Heating is continued until starch is no longer present, and the hydrolysis is considered complete. The main reaction ultimately obtained may be represented thus—

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6,$$

but it takes place in stages, and is far more complex than

appears from this equation.* Smoothness of conversion is favoured by using a dilute acid (*e.g.*, 0·5 per cent.), but the process is then slower than with a more concentrated solution. A temperature above 100° C. hastens the conversion, but involves risk of caramelisation. Hydrochloric and oxalic acid may be used as inverting agents in place of sulphuric acid, but the last-named is generally employed on account of its cheapness and its ease of removal subsequent to the conversion of the starch.

After treatment with sulphuric acid, the liquor containing the dextrose is neutralised with chalk made into a cream with water, the calcium sulphate is separated by means of a filter press, and the filtrate decolorised by animal charcoal (p. 178), and concentrated in a vacuum pan. Care must be taken to eliminate any trace of alkali before concentration, as dextrose is readily attacked by alkaline substances. The starch sugar thus prepared contains about 70 per cent. of dextrose, 5 to 10 per cent. of dextrine, and 10 to 20 per cent. of water; small quantities of maltose, ash, and indeterminate organic matter being also present. For most uses to which dextrose is put—*e.g.*, as a source of alcohol in beer and other fermented liquors—it is not required pure. When pure dextrose is required, it has to be crystallised from methyl alcohol, as its separation from its mother liquor cannot be effected by means of a centrifugal machine in the manner adopted for sucrose, the crystallisation of which takes place more readily than does that of dextrose. Much crude dextrose is used in preparing sweetmeats and factitious honey. Lack of sweetness is compensated for by the addition of saccharine (*q.v.*). Dextrose is also used for making **caramel**, which is prepared by evaporating a slightly alkaline solution of starch sugar to dryness, and heating to 220° C. = 518° F., or to a higher temperature when a product soluble in strong alcohol is required, as in the colouring of spirits. Beer, vinegar and sauces are commonly coloured by caramel obtained at the lower temperature, as the need for solubility in alcohol does not then arise.

2. **Lævulose** (*fruit sugar*), $C_6H_{12}O_6$, is the constant concomitant of dextrose when sucrose is inverted (*v.i.*). It has a rotatory power of $\alpha_D = -98{\cdot}8°$, this being greater than that of dextrose, and in a contrary direction. Thus, it follows that invert sugar consisting of equal parts of dextrose and lævulose is lævo-rotatory. Lævulose is somewhat sweeter than cane sugar. It has a small use medicinally for diabetic patients, and is prepared from invert sugar by taking advantage of the fact that the compound which it forms with lime, $C_6H_{12}O_6CaO.H_2O$, is sparingly soluble in water, whereas the corresponding derivative of dextrose dissolves readily. It is also formed on the hydrolysis of the starch-like carbohydrate *inulin*, $(C_6H_{10}O_5)_6.H_2O$.

* Dextrin is an intermediate product, and a portion is usually present in the crude dextrose ultimately obtained.

Invert sugar is prepared from sucrose by subjecting it to hydrolysis, the process being termed inversion, inasmuch as the dextro-rotation of the original sugar is changed into a lævo-rotation which is approximately the algebraical sum of the rotations of dextrose and lævulose. The hydrolysis of sucrose is readily effected by heating with a dilute acid. Even carbonic acid is capable of causing inversion. Invert sugar finds application in the preparation of sparkling wines, the after-fermentation taking place more easily with it than with sucrose (see *Champagne*, Vol. II., p. 208). Honey consists essentially of invert sugar, though the nature of the saccharine material supplied to the bees influences the product.

STARCH.

Starch, $(C_6H_{10}O_5)_n$, is a carbohydrate occurring abundantly in all plants. By far the greater part of the starch grown for consumption is used in the form in which it exists in cereals—*i.e.*, associated with fat, nitrogenous matter and mineral constituents. A fraction, however, which is absolutely large though relatively insignificant, is extracted from starch-bearing plants in a state of approximate purity, and used for special purposes (*v.i.*). Starch being a constant product of vegetation, its profitable extraction is naturally restricted to the treatment of a comparatively few plants exceptionally rich in starch, and yielding it with unusual ease. No rarity compels its winning from less facile sources. The composition of various typical starch-yielding materials is given in the following table:—

	Potato.	Wheat.	Maize.	Rice.
	Per cent.	Per cent.	Per cent.	Per cent.
Starch,	20·7*	70·0	68·4	76·5
Woody fibre,	1·4	2·5	2·5	0·6
Nitrogenous matter,	2·0	12·4	9·9	7·8
Fat,	0·2	1·7	4·6	0·9
Ash,	1·0	1·8	1·5	1·0
Water,	74·7	11·6	13·1	13·2
	100·0	100·0	100·0	100·0

Although no chemical difference, greater than can be ascribed to the influence of accompanying impurities, exists between starch of different origins, yet the size and structure of starch granules from dissimilar plants are very various, each being characteristic of the source whence the starch has been derived. Thus the average diameter of the starch granule of the arrow-

* When calculated on the substance containing 10 to 12 per cent. of water, the content is similar to that of the other materials quoted.

root is 0·140 mm., while that of the starch granule of rice is 0·022 mm. The differentiation of starches by size and shape of granule belongs to the province of analytical chemistry.

Manufacture of Starch.—The winning of starch from starch-bearing plants is mainly a mechanical process, consisting in comminuting the raw material, washing out the starch by suspension in water, and purifying it by levigation. Certain chemical principles are, however, involved, neglect of which is greatly detrimental to economy of working.

Potato starch serves as an example of a starch obtained by methods almost wholly mechanical. Potatoes are grown for starch making on the Continent, especially in Germany. They are liable to disease, which greatly diminishes the content of starch, and when stored tend to lose starch by vital oxidation, particularly if sprouting occur. When exposed to frost, a conversion of starch into sugar takes place, the well-known sweet flavour of a frost-bitten potato being due thereto. A rough works test of the content of starch is usually made by taking the specific gravity of 10 to 12 lbs. of potatoes, the specific gravity rising with the percentage of starch present, being about 1·08 with 14 per cent. of starch, and 1·14 with 27 per cent. The potatoes are well washed, and then pulped in a rasping machine, which consists of a rotating horizontal cylinder furnished with internal serrated blades, against which the potatoes are pressed. It is important that the cells containing the starch should be torn open, as otherwise the starch is not extracted in the subsequent processes. Even with the best modern raspers a loss of 20 to 25 per cent. of the starch is usually incurred. (A portion of this retained starch may be recovered by a second rasping process, or by grinding the rasped product after the bulk of the starch has been removed.) The pulp is washed upon brass wire sieves, and the starch is carried off in suspension in the water, the larger fibrous debris of the cells of the potato being left on the sieves. The liquid contains in suspension, besides starch, any fine sand from the potatoes and the finer debris of the potato cells, and in solution, salts, albuminous and non-nitrogenous extractive matter. It is run into collecting vats, well stirred, and run off, leaving the sand; thence it passes to settlers, in which it is allowed to remain for some hours. The layer first deposited is nearly pure starch, while upper and later layers contain such fibrous organic matter as has passed through the sieves during the washing of the pulp. The lower layer is white, whilst the upper is greyish in tint and can be scraped off and rewashed. Separation is better effected by centrifugal machines, which both drain the water off and segregate the starch and fibre in the manner of an ordinary centrifugal separator. The "green" starch, in the form of a slurry or paste, containing from 25 to 50 per cent. of water, according to the method of separation em-

ployed, is dried, first at a low temperature to prevent its gelatinisation, and finally at 60° to 70° C. = 140° to 158° F. As put on the market in an air-dried state it contains 16 to 18 per cent. of water.

A large proportion of commercial potato starch is not dried, but used at once in the "green" state for conversion into starch sugar by hydrolysis, in the manner described above (see *Starch Sugar*, Vol. II., p. 181). The residue left from the extraction of the starch still contains about 66 per cent. of its total dry weight of starch, together with small quantities of nitrogenous matter, and serves as a fodder of indifferent quality. The water from which the starch has been deposited in the washing process contains a trifling amount of mineral manurial constituents, such as potash and phosphoric acid, and some nitrogenous matter; it may, therefore, be utilised where irrigation is practicable.

Diseased potatoes are sometimes worked up for their starch by being subjected to a preliminary process of fermentation, similar to that described below for the production of wheat starch (*q.v.*).

Wheat Starch.—Starch may be prepared from wheat, either by opening up the grains of wheat by a spontaneous fermentative or putrefactive action, or by simple washing aided by treatment with caustic soda. According to the first method, the wheat is allowed to swell in water and is then crushed in bags, the starch being thus extruded and carried away by a stream of water. The water, containing starch in suspension, is run into tanks, where it remains for a fortnight or three weeks, during which time fermentation sets in at the expense of the gluten, which has accompanied the starch when it was first washed out of the grain. If the fermentation be controlled so that the putrefactive stage is not reached, the starch is but little affected, and can be separated and purified from gluten by systematic washing, in the manner already described for potato starch. The green starch is removed and dried in the usual manner.

Fermentation for removing the gluten can be dispensed with by using as a solvent for the gluten caustic soda of specific gravity 1·013, in such quantity as to keep the liquid always slightly alkaline. That portion of the gluten which is not dissolved by the caustic soda is removed by a fine-meshed sieve, while the portion in solution is washed away or precipitated as described under *Rice starch*. The yield of starch of good quality is higher than that obtained in the more primitive processes. The irregular sticks, roughly rectangular in section, which are generally preferred by the domestic consumer of starch, can be prepared by tightly wrapping a moist cake of starch in paper and drying the confined mass. Contraction sets in with approximate regularity, yielding sticks of the form familiar in the laundry.

Rice Starch.—The rice plant (*Oryza sativa*) may contain as

much as 80 per cent. of starch, and is thus a richer raw material than are potatoes or wheat, but on account of the refractory character of the gluten associated with the starch, the liberation of the starch granules needs to be effected by treatment with a dilute alkaline solution. Unless the solution be kept weak, gelatinisation of the starch may occur, and acids are inconvenient for opening up the grain, as their use makes that of metal machinery and fittings unsuitable. The raw material used for the manufacture of rice starch generally consists of the waste and broken grains obtained as a bye-product in dressing rice for consumption as a food. Typical material of this class contains about 12 per cent. of water, 76 per cent. of starch, 9 per cent. of albuminous matter, and small quantities of fat, crude fibre, ash, and carbohydrates other than starch itself. This material is placed in tanks provided with perforated false bottoms, and treated with caustic soda of about 1 per cent. strength. The liquor is run off after about eighteen hours, and the rice again treated with a fresh portion of caustic soda solution for a further period of twelve hours. It is then ground to the utmost possible fineness, the mass being ground while wet with the same dilute caustic soda solution. The milky liquid is then passed through sieves which retain a good deal of the swollen gluten, and afterwards run into tanks and allowed to settle, the starch being ultimately washed in a manner similar to that adopted with other raw materials (*v.s.*). The gluten contained in the washing waters can be precipitated by acidifying them, and used as a fodder.

Maize Starch.—According to Archbold an average sample of maize contains 11 per cent. of water, 55 per cent. of starch, 16 per cent. of woody fibre, 8 per cent. of albuminous matter, small quantities of carbohydrates other than starch, and nearly 5 per cent. of fat, and an equal quantity of ash. The large proportion of non-starchy materials, notably fat and gluten, renders the process of extraction of the starch somewhat complex. The manufacture is chiefly conducted in the United States, the process in use being known as the "sweet" process, the phrase thus differentiating it from the fermentative process for wheat, which is "sour." The preliminary treatment of the grain includes the removal of the germ, which is of considerable size, and disproportionately rich in fat. The maize is steeped in soft water for about a week, until, indeed, incipient putrification occurs, and the maize is sufficiently soft to grind. At this stage sulphuretted hydrogen is evolved from the maize, and in order to avoid this unpleasant product the steeping process is sometimes expedited by working at as high a temperature as 140° F. = 60° C., and allowing a continuous flow of water to pass through the softening tanks. A large quantity of matter is thus dissolved, and is generally run away as waste. The softened grain is finely

ground, and the starch separated from the residual gluten and woody fibre by passage through sieves. The starch passing in suspension through these sieves is run into a vat, allowed to settle, and treated with caustic soda in dilute solution. Some of the gluten is by this means dissolved, while another portion is precipitated, the starch being freed from both by the usual processes of subsidence and elutriation. Care has to be taken to keep the liquid in the settling vats cooled, lest fermentation set in. The starch is finally allowed to settle, and is dried in the manner already mentioned.

Various starches are prepared for eating from special plants, such as the arrowroot (*Maranta arundinacea*), the root known as **cassava** or **manioc**, and the pith of various palms, the finished product of which is known as **sago**. Save for greater care in preparation, designed particularly to obtain a white product, the preparation of these edible starches differs in no essential respect from that of those which have been already dealt with.

The slightly yellow tint of ordinary starch is generally hidden by the addition of a small quantity of a blue colouring matter, such as ultramarine. The uses of starch may be divided into two classes. The first class includes all those uses which depend upon its chemical status as a carbohydrate. The preparation of starch sugar, and the consumption of starch as a food are the chief examples of this class. The second main class of uses to which starch is put, depends upon the fact that starch products are pre-eminently colloidal, their solutions having a high viscosity and considerable adhesiveness. These qualities are taken advantage of in the dressing of textile materials, and in thickening colouring matters for calico-printing. Starch itself is incapable of acting as a stiffening or glutinous material, because it is perfectly insoluble in water or any other solvent. When heated with water, however, the starch granules swell and yield a gelatinous mass known as starch paste. A small quantity of starch thus heated to the point at which the swelling of the granules occurs, is capable of forming a coherent jelly with a large quantity of water, the phenomenon being apparently identical with that observed in the case of gelatin. The chief educts of starch which are of commercial importance may be conveniently dealt with as follows:—

Dextrin or **Dextrine** (*British Gum*).—The term dextrin is applied somewhat loosely to the earlier products of the hydrolysis of starch. The sugar yielded by the action of diastase on starch is maltose (p. 181), and at one time dextrin was supposed to be a single substance, intermediate in composition and chemical locus between starch and maltose. It is now, however, generally conceded that dextrin and maltose are produced concomitantly from the hydrolysis of starch, and that at least two dextrins are to be distinguished; they are characterised by their behaviour with

iodine, one giving no colouration, while the product of the other is red (see further, p. 197). Commercially, dextrins are not classified in this manner, but are differentiated by their respective methods of preparation. The first method of manufacture consists in roasting dry starch at a temperature of 220° to 250° C. = 428° to 482° F., either over a direct fire, or, better, in an oil bath, or by superheated steam. Revolving roasters are often used. The process is continued until the starch has acquired a brownish colour and has become soluble in water. The second method is carried out by moistening the starch with about 1 per cent. of hydrochloric or nitric acid, and slowly heating it in open dishes until a temperature of about 100° C. = 212° F. has been reached, and the acid has been evaporated. The sugar accompanying dextrin made by the use of an acid is dextrose. Dextrin made in this manner is lighter in colour than that obtained by direct roasting, and is thus better fitted for certain uses. On the other hand, any residual trace of acid is an objection for many uses. A special grade of dextrin of light colour, and having the translucent appearance of gum arabic, is also manufactured as a substitute for natural gum.

The chief uses of dextrin are for purposes in which its viscosity and adhesiveness are of value—*e.g.*, as a gum substitute (mentioned above), for stiffening textile materials, for giving a gloss to paper and cardboard, and producing a "head" on beer and aërated liquids.

CHAPTER IX.

BREWING AND DISTILLING.

I. FERMENTATION. — General Principles.—The term fermentation originally meant an appearance of boiling due to the escape of gas from a liquid, but it has acquired a wider significance, and includes the various chemical changes induced by the presence of some nitrogenous organic product or micro-organism, which is called a **ferment.** This class of chemical change is essentially characterised by the fact that a very large amount of material is affected by an inconsiderable quantity of the ferment. Ferments are of two kinds, **unorganised** and **organised.** The former are definite chemical compounds, of the character of albuminoids, and are not living organisms; they produce changes which are, as a rule, simpler in character than those caused by organised ferments, and are often of the nature of the change called hydrolysis, which is also brought about by such agents as dilute acids. Unorganised ferments are termed **enzymes.**

An instance of the action of an enzyme is afforded by the conversion of cane sugar (which rotates the plane of polarisation to the right), by means of the enzyme **invertase,** into a mixture of dextrose and lævulose (which turns the plane of polarisation to the left), the process being accompanied by the assimilation of water (*Hydrolysis*, p. 183).

In the case of the organised ferments, the decomposition is more profound, and up to the present appears to be the direct effect of the life of the organism, inasmuch as it has hitherto not been dissociated from the living cell. The change is, however, supposed by some to be due to the action of an enzyme which has been formed by the living cell. The best example of such decomposition is that afforded by yeast, which is more fully discussed later. The ordinary organised ferments are generally classified into *moulds* or *fungi*, *saccharomycetes* or *yeasts*, and *schizomycetes* or *bacteria*. The effect of the first of these is illustrated by the fermentation of alcohol into acetic acid in the brewing of vinegar, that of the second by the fermentation of sugar into alcohol, that of the third by the fermentation of milk sugar into lactic acid (*q.v.*). It must be understood that the very large variety of organised ferments renders it difficult to identify

any one species with any particular fermentation, several being usually present in any fermentable liquid. Moreover, inasmuch as these microscopic organisms can be transmitted in the floating dust of the air, a fermenting liquid containing a single kind speedily becomes contaminated with others, unless the air having access to it be filtered. This doubtless serves to explain why special districts produce special fermentations. Certain organised ferments flourish in air and are killed by its exclusion; they are, in consequence, called *äerobic*, while others having the reverse properties are termed *anäerobic*. This question belongs to the domain of biology rather than to that of chemistry.

II. **BEER.**—Beer may be considered as a dilute solution of alcohol and albuminous matter, obtained by the action of yeast on saccharine material, flavoured by an innocuous bitter principle.

(A.) **RAW MATERIALS.**—1. **Amylaceous and Saccharine Matter.**—Beer was originally made by malting barley and fermenting its aqueous extract. The substance in barley capable of yielding alcohol is starch, which, however, is not directly fermentable, but has to be converted into sugar; this is effected by malting. When this fact was fully realised, it became customary to economise barley by substituting sugar from other sources. Moreover, inasmuch as more of the active principle (**diastase**) which converts the starch into sugar, is produced during malting than is necessary for the conversion of the starch in the barley itself, more amylaceous matter may be added in the form of unmalted barley, and thus part of the expense of malting saved. Consequently, brewing no longer consists merely in fermenting the aqueous extract of malt.

Malt.—For satisfactory malting a well-developed barley is essential, as only such has a high content of starch, and will germinate well. Good barley has the following characteristics:—It is light-yellow in colour, the grains are dry, even in size and have thin husks, and it is free from bacteria and moulds.

Malting is generally carried out as a separate trade from brewing, and consists of the following main processes:—(1) **Steeping.**—The barley is slowly run into a cistern of iron or cement filled with water, which must be clean and free from organic impurity; the sound grains sink to the bottom, while the unsound grains (together with dirt and dust) can be skimmed off the surface and used as cattle food. The water is changed every twelve to twenty-four hours, the process lasting altogether forty to seventy hours. The object of the process is to supply sufficient water for the subsequent germination. Frequently the barley, when taken out of steep, is placed in a *couch* or heap to keep in the heat of germination, and thus aid the process. (2) **Flooring.**—The steeped grain is spread on the malting floor, which is preferably of concrete, to a depth of 3 to 12 inches, according to the temperature, which should not exceed 12°

C. = 54° F. On this account malting is difficult to practise in the summer.

After the first twenty-four hours the grain is "ploughed," or turned over, twice a day for two or three days. When the **acrospire** or plumule of the grain has grown to a length of about three-quarters of the length of the grain itself, the rootlet is about twice the length of the grain, and the grain itself has attained a proper degree of "mealiness," this portion of the process is completed. During this operation, the grain is kept moist by periodical sprinklings with water.

An improved method of malting is that known as **pneumatic malting**, inasmuch as better control over the supply of air and moisture to the germinating grain is afforded. On the **Saladin system**, which may be taken as typical, the steeped barley is run into rectangular iron germinating cases with perforated false bottoms, where it is allowed to heat as in a couch. When it is desirable to check the heating, air which has been forced over cylinders that are kept wet is driven under the false bottom. Oxygen is thus supplied to the grain, carbon dioxide (a product of the vital processes) is removed, and the temperature is regulated. Subsequently, the grain is stirred by means of agitators. When germination has reached the proper point, the grain is elevated to the malt kiln. (3) **Drying.**—The germinated barley is called **green malt**, and contains the maximum amount of diastase, so that if this alone were needed the grain would be ready for the brewer; but a desiccation at a high temperature is essential, both for arresting the germination and for killing any mould or fungoid growths that may have appeared, and also for developing certain changes which impart flavour to the resulting beer. Dried malt can also be stored, and is more easily ground than green malt. The temperature of the drying kiln determines whether the malt shall be "pale," "medium," or "high-dried," each kind being used according to the class of beer to be produced. The malt is spread out to a depth of 8 to 10 inches on the floor, which consists of a series of perforated earthenware plates built in a kiln of square section, and heated by a number of baskets of live coke suspended beneath. Each kiln may contain several floors, two being a usual number, and the malt is loaded first on to the top floor, where it is dried at 120° F. = 49° C. until some 90 per cent. of the moisture is gone, then dropped through on to the lower floor, where it is dried at 180° to 190° F. = 82° to 88° C. This applies to pale malts. Medium and high-dried malts are finished at 200° to 230° F. = 93° to 110° C. (4) **Screening.**—The rootlets of the dried malt are removed by being trodden by men, and subsequently passed over a "water-fall" malt screen, which also removes dust. The finished malt is stored in bins, due attention being paid to the exclusion of moisture. Malt which has absorbed water, or become "slack," yields an unsatisfactory beer, and is generally re-dried before use.

The chemistry of the production of green malt resolves itself into the chemistry of germination. The proximate constituents of barley are—(1) Water; (2) carbohydrates,* including starch as the main constituent (39 to 57 per cent.), dextrin, α-amylan (2 to 4 per cent.), gum (3 per cent.), cane sugar (1·5 per cent.), extractives soluble in water, and cellulose the largest constituent of the woody fibre; (3) fat; (4) albuminoids, including mucedin, fibrin, casein, and albumin, together with the ferment diastase; (5) ash, consisting of the bases potash, soda, lime, magnesia, ferric oxide, and the acid-radicles of phosphoric, sulphuric, silicic acids and chlorine. The proportions of these constituents are shown by the following analysis, beside which is given one of pale malt:—

	Barley.	Malt.
	Per cent.	Per cent.
Water,	14·05	5·83
Carbohydrates,	63·66†	65·38‡
Woody fibre,	7·09	11·57
Fat,	2·05	1·65
Albuminoids,	10·58	13·09
Ash,	2·57	2·60
	100·00	100·12

Barley for brewing should be rich in carbohydrates and poor in albuminoids, of which a fine malting barley should not contain more than 8 to 9 per cent. The germination of barley produces a change in the nature of the albuminoids and a consequent change in the carbohydrates. The diastase naturally present in barley differs from that produced from the albuminoids during germination in that it cannot liquefy starch paste, but it resembles the latter in respect of its power to convert starch which has been already liquefied or rendered soluble, into maltose and dextrin. The diastase of malt is thus of two kinds, that which existed in the barley, and that produced by germination, and it is the production of the latter which is the object of malting, for it is able to transform the starch directly into maltose and dextrin. The nature of the change that produces this substance is not well understood. The quantity produced is relatively small—about 2 per cent.—and is measured by the "diastatic power" of a watery extract of the malt. By this term is meant the amount of maltose pro-

* These include carbohydrates of the pentose type—general formula $C_5H_{10}O_5$, or some multiple of this. These bodies are not fermentable by yeast, and to a large extent remain in the "brewer's grains" (*q.v.*).

† Mainly starch.

‡ About one-third of this is fermentable sugar.

duced by the action of the malt extract on starch, this being measured by the reducing effect of the resulting solution upon Fehling solution (an alkaline solution of cupric tartrate). Thus, the diastatic power of a malt extract is said to be equal to 100 when 0·1 c.c. of the extract of 25 grms. of malt in 500 c.c. of water converts sufficient starch paste into maltose to reduce 5 c.c. of Fehling solution (Lintner's standard). Diastase may be isolated from malt by extraction with 10 to 30 per cent. alcohol, precipitation of the clear filtrate after the elapse of eight hours with absolute alcohol, dissolution of the precipitate in water and re-precipitation with alcohol. When thus prepared it is a white amorphous substance, not perfectly definite in composition, but containing approximately—

C,	44·33	per cent.
H,	6·98	,,
N,	8·92	,,
S,	1·07	,,
O,	32·91	,,
Ash,	4·79	,,
	100·00	,,

Although diastase forms a small quantity of sugar from starch in the grain itself, yet its chief action takes place in aqueous solution during mashing (*q.v.*). The production of "mealiness" in malt, which has been attributed to the change of the starch, has been shown by Brown and Morris to be due to the disappearance of the cell-walls of the starch granules. During malting a small portion of the starch is completely burnt to H_2O and CO_2, a rise of temperature resulting.

The action of diastase is weakened by heating to 65° to 70° C. = 149° to 158° F., or by separation from the grain by treatment involving precipitation with alcohol, as described above. Its solutions are partly coagulated at 75° C. = 167° F. (like those of albumin), and its activity diminished. Its power is not, however, wholly removed even by drying at 100° C. = 212° F. Antiseptics, such as many metallic salts and bodies like salicylic acid, also restrain its action, diastase being similar in this respect to organised ferments.

Malt Adjuncts.—As has been already mentioned, the maximum effect is obtained from the diastase of malt by causing it to saccharify other starch than that of its parent barley. Such are the starches of maize, rice, and, for "white beer," wheat. It is more usual to add sugars to the wort (*q.v.*), in which they are fermented together with the maltose of the malt. The sugars generally employed are cane sugar, invert sugar—which is most largely used—and glucose. Refined cane sugar has to be inverted by the yeast before fermentation, and to a certain extent weakens

the yeast, favouring the production of lactic acid, so that it is preferable to invert the sugar first. Concerning the production of these sugars see Chap. VIII. of this volume.

2. **Hops and Bitter Principles.**—Of these, the bitter principle of hops is the chief and only legitimate bitter used in beer. Hops are the female flower of the plant, *Humulus lupulus*; the male flowers being useless, the plant bearing them is not cultivated. The proximate constituents of hops are fibrous matter (woody fibre), nitrogenous substances, sugars, gums, lupulin or "hop meal," tannin, and mineral matter. The constituents that are of importance for brewing are the lupulin and tannin. The former is a yellow resinous dust that can be separated from the hop flowers by sifting, and consists of glands which contain the essential oils and bitter principles, such as resinous alkaloids. It is technically known as "hop flower" or "condition," and is undoubtedly the essentially useful portion. In quantity it ranges from 5·3 to 17·5 per cent., and in the best hops should approximate to the latter number. The essential oil amounts to 0·25 to 0·35 per cent., the quantity diminishing as the age of the hop increases. The aroma of the hop is apparently due to these oils. The chief bitter principle of the hop is the resinified product of lupulic acid. Lupulic acid is not in itself bitter, but the resins produced by its oxidation have a strong bitter taste. This and the other resins which are present in hops appear to have an antiseptic action which hinders secondary fermentations, and they are thus useful in preserving the beer. Concerning the alkaloids but little is known; hopeïne, choline and traces of morphine are said to be present. The tannin in hops varies from 1·5 to 5 per cent.; it is doubtless useful in the copper (*q.v.*) for precipitating albuminous matter. The hops, after picking, are dried in a kiln resembling a malt kiln, and frequently "sulphured" by burning 1 to 2 per cent. of sulphur in the kiln, to bleach them should they be of a bad colour. In judging such hops allowance must be made for the possible defects thus concealed, the colour of the hops being a considerable criterion of their value. Where hops are added to the beer in cask, the sulphur dioxide is liable to become reduced to sulphuretted hydrogen, producing "stench." The practice of sulphuring is easily detected by analysis. The sprinkling of flowers of sulphur on the hops during their growth to destroy parasites is less objectionable.

Hop substitutes are used for the sake of cheapness. Those commonly employed are gentian, camomile and quassia. Their use is illegitimate.

3. **Water.**—The water used both in the preparation of malt and in actual brewing should be free from contamination with organic matter and from the micro-organisms that occur in impure water. The next most important consideration in regard

to the water is the quantity and nature of the mineral matter dissolved in it. When this consists largely of gypsum (calcium sulphate), the water is well adapted for the production of pale ale, and it is on this account that the Burton water is famous. Those waters which contain too little gypsum for brewing pale ale are successfully applied for the production of mild ale. Waters containing no gypsum, but rich in alkali sulphates and carbonates, are adapted for producing black beers. The following analyses illustrate these differences:—

	Grains per Gallon.		
	Pale Ale.	Mild Ale.	Black Beer (Stout).
$CaSO_4$, ...	40	25	0
$MgSO_4$, ...	8	5	0
$CaCO_3$, ...	15	15	3
$MgCO_3$, ...	...	...	1·5
K_2SO_4, ...	10	5	7
K_2CO_3, ...	...	...	9·5
Na_2CO_3, ...	...	...	6·5
$MgCl_2$, ...	5	3	...
NaCl, ...	30	20	15
SiO_2, ...	...	...	0·5

The mild ale type of water is a fairly common one, so that such beers are brewed in many districts. The London deep-well water is of the third type, and produces good black beers; but since the knowledge of the characteristics necessary in waters for definite beers has been acquired, the waters of the second and third type have been transformed into waters of the first class by the addition of the requisite amount of gypsum. To change waters of the third type into those of the second, gypsum and kainit* are added. To produce water of the first class from a neutral water (one containing no sodium carbonate), it is only necessary to add calcium sulphate to the water ("burtonising"), which can be conveniently effected by running the water through a wooden vat provided with a false bottom and packed with small lumps of gypsum, care being taken that the gypsum dissolved by the water shall be regular in amount. It is frequently necessary to add more magnesium sulphate and calcium chloride. In treating a water of class three, the alkaline carbonates must be removed by the addition of calcium chloride, which forms calcium carbonate and sodium chloride. The subsequent treatment is the same as for class two. The influence of the salts dissolved in a water in the brewing process will be referred to on p. 199.

* A mineral composed of potassium sulphate, magnesium sulphate, magnesium chloride and water, frequently mixed with sodium chloride.

4. **Yeast.**—This is more conveniently dealt with under the head of processes of beer manufacture (see also *Fermentation*, Vol. II., p. 189).

(B.) **PROCESSES.**—1. **Mashing.**—The first step in the preparation of a beer is the production of the liquor to be fermented, called the **wort.** For this purpose the malt is first ground between smooth steel rollers, the object being to crush but not to powder the grain, so that the meal may be readily separated from the husk. The ground malt or **grist** falls from the rollers into a grist case, traversing in its passage a magnetic separator, which removes particles of iron incidentally present. The grist then falls into a cylindrical vessel set horizontally, where it meets the water previously heated to 160° to 170° F. = 71° to 77° C., and is thoroughly mixed with the water by means of an agitator consisting of a horizontal shaft carrying spokes which just clear the walls of the cylinder. This apparatus is known as a **Steel's masher.** From this vessel the malt passes to the mash tun, which may be 18 feet in diameter by 8 feet deep, and may serve for the mashing of 100 quarters of malt; it is an oaken vessel provided with a perforated false bottom and with a vertical shaft actuating arms carrying rakes which keep the contents of the tun in motion. The same shaft serves to carry the **sparger,** which consists of a set of perforated radial arms through which water is supplied for washing the malt (**sparging**). The mash tun is fitted with "underlets" for the admission of water below the false bottom. A number of draw-off pipes are also provided. When all the grist has entered the tun, the residue from the Steel's masher is washed into the tun, and the temperature of the mash ascertained. Should this be below 140° F. = 60° C., hot water is introduced through the underlet to bring it to between 140° to 150° F. = 60° to 66° C. The tun is covered, and the mash allowed to stand for about two hours. Should the starch of the malt be difficult to liquefy and saccharify, a second mashing is made by the admission of fresh water through the underlet. The wort is drawn off almost completely, and the exhaustion of the malt finished by sparging with hot water through the pipes referred to above. This process is continued until the specific gravity of the wort is 1·005. According to the practice of some continental breweries, a portion of the malt is boiled with water and returned to the mash tun, this process being twice repeated, instead of infusing the malt with hot water, as described above.

In the process of mashing, the diastase of the malt converts the starch into maltose and dextrin. Inasmuch as ordinary starch is insoluble in water, it must first be rendered soluble before it can be hydrolysed. This is effected by the particular form of diastase characteristic of malt, as distinct from that of barley. The soluble starch is then converted into **malto-dextrin**

and **erythro-dextrin.** An equation representing this change is—

$$(1)\quad \underset{\text{Soluble starch.}}{5(3C_{12}H_{20}O_{10})} + H_2O = \underset{\text{Malto-dextrin.}}{\begin{cases} C_{12}H_{22}O_{11} \\ 2C_{12}H_{20}O_{10} \end{cases}} + \underset{\text{Erythro-dextrin.}}{4(3C_{12}H_{20}O_{10})}.$$

The next action is the hydrolysis of malto-dextrin into maltose—

$$(2)\quad \underset{\text{Malto-dextrin.}}{\begin{cases} C_{12}H_{22}O_{11} \\ 2C_{12}H_{20}O_{10} \end{cases}} + 2H_2O = \underset{\text{Maltose.}}{3C_{12}H_{22}O_{11}}.$$

The erythro-dextrin undergoes a change by assimilation of water into malto-dextrin and **achroo-dextrin**—

$$(3)\quad \underset{\text{Erythro-dextrin.*}}{4(3C_{12}H_{20}O_{10})} + H_2O = \underset{\text{Malto-dextrin.†}}{\begin{cases} C_{12}H_{22}O_{11} \\ 2C_{12}H_{20}O_{10} \end{cases}} + \underset{\text{Achroo-dextrin.*}}{3(3C_{12}H_{20}O_{10})}.$$

The malto-dextrin is converted into maltose as in equation (2). The achroo-dextrin is further converted into malto-dextrin by the assimilation of water, and this in turn into maltose. The final products, under ordinary conditions of mashing, appear to be maltose and an achroo-dextrin, $3C_{12}H_{20}O_{10}$, less complex in grouping than that produced in the earlier stages. The precise reactions occurring during mashing are regulated by the temperature prevailing and the rapidity with which the temperature is raised. As soon as the temperature rises to 140° F. = 60° C., the action of the diastase begins to be checked, and this restriction means that much of the malto-dextrin suffers no further alteration. Such as remains is not directly fermented by the yeast in the fermenting vat (*q.v.*), but suffers fermentation in the cask, producing beneficial effects on the beer. The proportion of starch converted into maltose is about four-fifths of the whole, the rest being present as dextrin.

2. **Boiling.**—The wort, cleared by running through the spent malt (**brewer's grains**), flows from the mash tun either directly into the copper, or into an intermediate vessel ("underback"), in which, however, it must not remain long enough for its temperature to fall appreciably. While the copper is being filled the fires are lighted, so that the temperature may be kept up, and the hops are added in proportion, varying from 10 to 20 lbs. per quarter of malt in the wort, according to the character of beer to be produced, and if any other saccharine matter than malt is to be added it is also introduced at this stage. The hops are added *pari passu* with the malt, a final dose being used just before the completion of the boiling, so that the whole of the aroma is not lost by evaporation. The boiling generally lasts

* Erythro-dextrin and achroo-dextrin are so called because they give red and colourless products respectively when treated with iodine.

† This composition must be taken only as representative of the class of bodies known as malto-dextrins, as their exact composition varies with the conditions of formation.

from two to three hours, and during the process all diastatic action is stopped, and a large proportion of soluble albuminoids becomes coagulated and precipitated. The proportion of maltose and dextrin in the wort is determined by ascertaining the specific rotatory power by the polarimeter* at various stages of the boiling. The wort is generally boiled on an open fire, but sometimes by closed steam, which must be of high pressure to give a sufficient temperature to boil thoroughly, and to sterilise the wort in order that the beer may be sound.

3. **Cooling.**—The wort from the coppers is run into "hop-backs," in which it is drained from the exhausted hops, these being afterwards sparged to remove the adhering wort. It is then cooled by exposure to a good draught in shallow tanks (coolers), and then passed over vertical refrigerators, consisting of copper pipes through which water is circulated. In ordinary English practice the temperature has to be reduced to 58° to 60° F. = 14° to 16° C. in the course of six hours for the whole of one brewing. Cold spring or well water suffices for this. In Germany, where bottom fermentation (*q.v.*) is in vogue, the temperature is lowered to 5° C. = 41° F., and for this purpose the lower parts of the refrigerators are supplied with water, the temperature of which has been reduced to near 0° C. = 32° F. by means of freezing machines. During cooling not only is the temperature lowered to the point suitable for fermentation, but the wort is also aërated, and a certain amount of albuminous matter (known as "cooler grounds") deposited. While the hot wort is cooling in the coolers—as distinct from the refrigerators—the oxygen which is taken up chemically changes some of the resins from the hops, causing them to coagulate into particles which sink readily and thus carry down suspended matter, clarifying the wort. On the refrigerators the air is dissolved and serves for the respiration of the yeast in the subsequent fermentation. The infection of the wort with bacteria and wild types of yeast, derived from the floating matter in the air, during cooling, is to be avoided as much as possible, and it has been proposed to supply sterilised air to the refrigerating rooms. The average composition of the air-dried solid matter in wort from medium dried malt, may be taken as represented by the following figures :—

	Per cent.
Maltose,	57·01
Dextrin,	14·92
Lactic acid,	0·56
Soluble albuminoids,	2·09
Colouring matter, ash, &c.,	1·49
Total dry solids,	76·07

* For the construction and use of the instrument, see Allen's *Commercial Organic Analysis*, vol. i., pp. 16, 194.

The influence of the water used for mashing and boiling (*q.v.*) is very considerable. The calcium and magnesium carbonates in the water are, to a certain extent, thrown out of solution during the preliminary heating, and, remaining in suspension, effect the neutralisation of sundry organic acids (such as lactic) which are present in the malt. The presence of calcium sulphate is beneficial in causing the precipitate of albuminous matter which is produced during boiling, to take a flocculent instead of a pulverulent form, and thereby to be more easily separable. The objection to alkali carbonates in a water for mild or pale ale is that injurious nitrogenous matters are liable to be dissolved by their aid. Much colouring matter is extracted from the malt by alkaline waters, and this is the reason of their use for black beer.

Certain excessively bitter resins from the hops are also extracted by alkaline waters. Sodium chloride is a very beneficial constituent of a brewing water, exercising an antiseptic action during fermentation, and influencing the flavour of the finished product.

4. **Fermentation of the Wort.**—The cooled wort is run into fermenting tuns,* which are large wooden vats provided with coils of pipes (**attemperators**) through which either warmed or cooled water may be circulated to regulate the temperature of the wort. When a portion of the wort has been run in, the yeast is added, in the proportion of 1 to 4 lbs. per barrel of wort, the quantity depending upon the quality of beer to be brewed, strong beer needing most yeast. This process is known as "pitching" the wort. The rest of the wort is then run in, and the temperature (which is to begin with 60° F. = 16° C.) allowed to rise by the action of the yeast to about 70° F. = 21° C., which it should attain at the rate of about 1° F. in 6 hours. This rate must be maintained by the use of the attemperators. The surface of the wort during fermentation becomes covered with a froth consisting of yeast, in "top fermentation" according to English practice, blown up with carbon dioxide. The appearance and motion of the froth serve the brewer as an index of the progress of the fermentation. As the conversion of the maltose into alcohol and carbon dioxide proceeds, the specific gravity of the liquor falls, and the wort is said to "attenuate." When the above-mentioned temperature (70° F.) has been reached, the attenuation will generally be about one-half—*i.e.*, a wort of specific gravity 1·050 will have become attenuated to 1·025. The closest attention on the part of the brewer is required during the process of fermentation, temperature and specific gravity having to be carefully noted. Fermentation is generally

* Owing to excise regulations in this country, the wort is first received in a collecting vessel until the volume and specific gravity have been ascertained by an excise officer.

complete in two or three days. In making lager beer according to German practice, "bottom fermentation" is employed, the name implying that the yeast grows at the bottom of the fermenting tun. For the proper execution of this process, a temperature of 5° to 6° C. = 41° to 43° F. should not be exceeded, on which account the fermentation is either conducted in cellars or in rooms artificially cooled, whereby the manufacture can be continued throughout the year.

The general principles of fermentation have been already explained (p. 189). The conversion of sugar into alcohol is effected by organised ferments, of which the *Saccharomycetes* are the most important. The best known of these are those composing the usually complex mixture called *yeast*, and the *ginger-beer plant*, which has recently been shown by Marshall Ward to be a symbiotic association of a yeast and a bacterium. The alcoholic fermentation induced by this plant appears to be the work of the yeast, but this is aided by the bacterium, the former being enabled to carry the fermentation further by reason of the removal of inhibiting products by the bacterium. The aid thus afforded is what is implied by the term symbiosis, for all yeasts are ultimately killed by their own products. Yeasts are single-celled vegetable organisms, which multiply either by budding (gemmation) or fission (formation of *ascospores*; endogenous division). Of these two methods of reproduction that by gemmation appears to be normal; if nourishment be scanty, ascospores are formed. Like other plants, yeast must be provided with the mineral matter constituting its ash. This is found in sufficient quantity in ordinary wort, in which is a proportion of the mineral constituents of the barley whence it is derived. The wort also contains much sugar and some nitrogenous matter, and is a suitable medium for the rapid growth of the yeast. The composition of yeast (bottom yeast) is shown by the following analysis:—

	Per cent.
Cellulose and mucilage,	37
Albuminoids,	36
,, soluble in alcohol,	9
Peptones,	2
Fat,	5
Extractive matters (leucin, glycerol),	4
Ash,	7
	100

These results refer to the dried material.

Fresh yeast contains from 40 to 80 per cent. of water. The composition of the ash differs slightly, according as the yeast is for top or bottom fermentation.

	Top.	Bottom.
K_2O, ...	38·8	28·3
CaO, ...	1·0	4·3
MgO, ...	6·0	8·1
P_2O_5, ...	53·9	59·4
SiO_2, ...	Trace	0

The rationale of the conversion of sugar into alcohol by yeast is still uncertain. The explanation most commonly accepted rests on the assumption that sugar is broken down into alcohol and CO_2 in the yeast cell; the other having most claims to consideration consists in the view that the decomposition of the sugar is effected by molecular vibration, set up by the protoplasm (or living nitrogenous contents) of the yeast, and extending a short distance beyond the yeast cell. In any case the main reaction is represented thus:—

(1) $\underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + H_2O = \underbrace{\underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6}}_{\text{Invert sugar.}}$.

(2) $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$.

Whatever sugar is used by the yeast it is first converted into dextrose and another sugar of the same series. Thus, cane sugar, of which maltose is an isomeride, becomes converted into dextrose and lævulose, and milk sugar into dextrose and galactose. Both these products are fermented, but the dextrose undergoes the change more rapidly. The reaction represented in equation (1) is called "inversion," and is effected by a soluble unorganised ferment secreted by the yeast, called **invertase**; the quantity of sugar which the yeast will ferment is independent of the original nature of the sugar—that is to say, the organism is not impoverished in fermentative capacity by having to effect the inversion of the sugar. The fermentation is invariably accompanied by the formation of secondary products, chief among which are glycerin and succinic acid. 100 parts of cane sugar yield 105·36 of invert sugar, and are fermented to the following products:—

	Per cent.
Alcohol, ...	51·11
CO_2, ...	49·42
Succinic acid, ...	0·67
Glycerin, ...	3·16
Cellulose, fat, &c., ...	1·00
	105·36

The simplest equation representing the production of the bye-products is—

$$4C_6H_{12}O_6 + 3H_2O = \underset{\text{Succinic acid.}}{C_4H_6O_4} + \underset{\text{Glycerin.}}{6C_3H_8O_3} + 2CO_2 + O.$$

The oxygen serves for the respiration of the yeast. It appears that the purer the yeast the lower the proportion of bye-products formed, but they are never absent. The formation of alcohols higher in the series than ethyl alcohol—collectively known as fusel oil—occurs to some extent in the fermentation of wort, but it is doubtful whether they are the products of the action of pure yeast (*Saccharomyces cerevisiæ*) or of adventitious varieties.

For the most rapid propagation of yeast certain conditions must prevail—*e.g.*, the percentage of sugar in the nutrient liquid should lie between 2 and 4, and the temperature must range between 25° and 30° C. = 77° to 86° F.; should the percentage of sugar exceed 35, or the temperature rise above 35° C. = 95° F., or fall below 0° C. = 32° F., the growth of the yeast will be arrested; the carbon dioxide evolved also serves to some extent as a retarding agent. When the percentage of alcohol in the fermented liquor exceeds 20, the growth of the yeast is also inhibited. In perfectly pure sugar (free from nitrogenous matter and ash), the yeast will only grow by feeding on the nutrient matter it already contains. *Saccharomyces cerevisiæ* exists in two forms, that characteristic of top fermentation, already described, and that producing a bottom fermentation, used for lager beer, which is now brewed to some extent in this country as well as in Germany. Bottom yeast consists of round or oval cells, 8 to 9 μ* in diameter, which are slightly smaller and less aggregated and branched than top yeast. Its mode of reproduction is, however, similar. It is active at 4° to 10° C. = 39° to 50° F., and during the fermentation it collects at the bottom of the tun. Before modern brewing methods, resting on a knowledge of chemical and biological principles, were generally adopted, brewers' yeast was a mixture of various saccharomycetes with moulds and bacteria, and the course of the fermentation, and therefore the quality of the product, were largely a matter of chance. Nowadays, the need for fairly pure yeast is recognised, and microscopical examination is used to judge of its quality. The cells should be of uniform size, plump, transparent, and without a granulated appearance. Dead cells and rod-like organisms (*Bacteria*) should be absent. The yeast is never entirely free from the latter, but certain standards are laid down.† In bulk, the yeast should have a rich cream colour and a clean sweet

* $\mu = \frac{1}{1000}$ mm.

† For detailed account see *A Text-book of the Science of Brewing*, by Moritz and Morris.

smell. A more systematic method consists in preparing pure cultivations of yeast. The principle upon which this depends is the approximate isolation of the organism to be cultivated from accompanying growths, in a flask of nutrient liquid which has been previously sterilised by boiling. When a microscopical examination of the yeast in each cultivation made, shows that the characteristics of *Saccharomyces cerevisiæ* predominate in any one of them, the growth of that cultivation is further encouraged in order to obtain a pure yeast for brewing. On a large scale pure yeast is sown in sterilised wort, the process being carried out in sterilised copper vessels, access of air to which can only take place through filters of cotton wool to exclude germs, and the growth of pure yeast thus obtained is used to ferment the beer in the tuns. This plan is not practised in this country, owing to Excise difficulties, but it is employed abroad, notably in Germany.

5. **Cleansing of the Beer.**—When the wort has reached the proper attenuation, the beer has to be freed from yeast. This is done by several methods, of which the chief are—(1) the "union" method, (2) the "skimming" system, and (3) the "stone square" system.

(1) The union method is an improvement on the old London cask method, which is used for beers that are to be consumed shortly after brewing. It consists in running the beer with the yeast into casks or "unions" holding 4 barrels apiece, and fitted with attemperators and a swan-neck pipe, opening over a trough common to a set of casks. The beer is run into the "feeding-back" and thence into the casks, where the fermentation continues, and the yeast rises, separates, and flows over through the pipe into the trough. The beer accompanying it is separated and returned to the feeding-back. After the fermentation is completed and the yeast ceases to flow over, the pipes are removed from the casks, and these are bunged up and allowed to settle. Among the advantages of this system are the exclusion of air during cleansing, the thorough separation of yeast due to the moderate size and shallowness of the vessels, and the fact that where it is practised the use of attemperators in the fermenting tuns is not essential, the beer being run into the unions as soon as it has reached a temperature of 70° F. = 21° C. (2) The skimming system consists in running the beer with the yeast into a "skimming-back," which is a large wooden tank provided with attemperators and fitted with large funnels of tinned copper ("parachutes"), the mouths of which are on a level with the surface of the liquid. The yeast is skimmed from the surface by a board into these funnels, and is thus removed. (3) The stone-square system consists in having two stone or slate vessels, one above the other, communicating by means of a manhole, which is provided with a collar about 6 inches high.

There is also a valve between the two vessels. The fermenting wort is run into the lower vessel, and is pumped at intervals into the upper one until the right attenuation is reached; at the last return the yeast will collect in the upper vessel, being prevented from reaching the lower one by the collar round the manhole. The yeast collected by any of these methods is washed, and the surplus above that required for the next "pitching" is pressed and sold, largely to distillers (see *Spirit*, Vol. II., p. 211). The yeast for pitching is used again as soon as possible, and in the interval should be kept cool and dry.

6. **Racking and Finishing Processes.**—The cleansed beer is occasionally run directly into cask, but the better plan is to employ a "settling" or "racking back." In this vessel the remaining suspended matter is deposited, and the beer may be here treated with a "priming" of sugar—which affords material for subsequent fermentation in the cask, and acts as a sweetening agent—be coloured with caramel (burnt sugar), and be preserved with antiseptics such as bisulphites, salicylic acid, sodium fluoride, &c. After the beer has been in the racking back for several hours, it is drawn off into trade casks, if for immediate consumption, or into storage casks or vats. In the former case it is clarified by the addition of "finings"—*i.e.*, isinglass dissolved in dilute sulphurous acid.* The isinglass forms a precipitate with the tannin of the beer, and in settling carries down suspended matter. The clarification of beer is sometimes aided by filtration through wood shavings; for these it has lately been proposed to substitute shavings of aluminium.

Beer in cask undergoes a secondary fermentation at the expense of residual malto-dextrin, and is thus aërated and kept in good condition. The finished beer is liable to various diseases, the chief of which are acetic fermentation induced by *Bacterium aceti* (see *Vinegar*, Vol. II., p. 219), which renders the beer sour, its action being favoured by access of air, and "ropy fermentation," probably due to the action of *Bacillus viscosus*. Such defects are largely produced by impure yeast and contamination of the beer by foreign micro-organisms; these causes are avoided by perfect cleanliness and the use of pure cultivations of yeast. Careful attention to the quality of water employed and proper treatment of the wort are also requisite. Details of such matters must be looked for in monographs on the subject. The following analyses (p. 205), by Graham, illustrate the composition of typical samples of beer.

During the secondary fermentation in cask, carbon dioxide is evolved, and imparts to the beer its characteristic effervescence; at the same time it serves to exclude air from the cask. In order to maintain these conditions, beer is often kept under pressure from a reservoir of liquid carbon dioxide, which also

* The practice of using sour beer as a solvent is to be condemned.

serves instead of a pump to raise it from the cellar for distribution. Much carbon dioxide is now recovered from the fermenting tuns, liquefied by pressure, and used for this and other purposes.

	Burton Mild Ale.	Burton Bitter Beer.	Dublin Stout, XX.	Pilsener Lager Beer.
Maltose,	2·13	1·62	3·45	0·69
Dextrin,	3·64	2·60	3·07	2·65
Albuminoids,	0·26	0·16	0·26	0·20
Lactic and succinic acids,	0·18	0·17	0·17	0·09
Ash, colouring matter, and hop extract,	0·53	0·87	1·76	0·59
Total solids,	6·74	5·42	8·71	4·22
Acetic acid,	0·01	0·01	0·01	0·02
Alcohol,	6·78	5·44	5·50	3·29

III. **WINE.**—Wine is an alcoholic liquor made by the fermentation of grape juice. The successful cultivation of grapes for wine production can only be effected in climates where the full proportion of sugar in the fruit can be obtained. Further, it appears that each country has a type of vine adapted for growth in it, and that vines do not flourish in a region other than that in which they originate. The grape is better adapted than any other fruit for the production of wine, because of the large content of sugar in the juice and the fact that a considerable proportion of the acid separates as potassium bitartrate after fermentation. The grape contains 95 to 97 per cent. of juice, which is a solution of sugar, organic acids, albuminous matter, mineral matter and extractive matter. The following figures (*Neubauer*) illustrate the proportion of these constituents in grapes of selected and of second quality:—

	Selected.	Second.
	Per cent.	Per cent.
Sugar,	18·59	16·35
Free acid,	0·53	0·60
Albuminoids,	0·25	0·26
Mineral matter,	0·29	0·27
Extractive matter,	4·71	4·21
Total solids,	24·37	21·69
Water,	75·63	78·31
	100·00	100·00
Specific gravity,	1·094	1·085
Ratio of acid to sugar,	1 : 35	1 : 27

When the grapes are beginning to ripen, the proportion of free acid to sugar is large, decreasing as the ripening proceeds. In unripe grapes, which are still sour, this ratio may be as high as 1 : 10, and malic acid is present, being eliminated as the grapes become ripe, while tartaric acid is not destroyed, but goes to form potassium bitartrate. The grapes must not be allowed to become over-ripe before being gathered, as they lose sugar by oxidation and are liable to be attacked by low growths, like moulds. Certain growths, however, though nourished at the expense of the sugar, are not altogether harmful, as their life-products impart an agreeable bouquet to the wine. Grapes are liable to various diseases in all periods of their growth, the most fatal of which are known as "oidium" and "phylloxera." These are combated by dressing the vines with various antiseptic compounds, such as sulphur and copper salts. The grapes are gathered, and if for red wine are picked from the stalks, because the stalks contain much tannin; this would be extracted during fermentation, which, for the sake of the red colour, takes place in contact with the skins, "marc." For white wines the juice is at once separated from the marc and stalks, thus avoiding separate picking. The juice is extracted in a press, or by passage through grooved rollers, care being taken not to bruise the seeds and stalks. A further quantity of juice is obtained by a second pressing. The percentage of juice ("must") is about 95 per cent. if the stalks have been removed, and 70 per cent. if they remain.

The fermentation of the must is allowed to take place spontaneously, and is effected mainly by the yeast named *Saccharomyces ellipsoïdeus*. The reason why the spontaneous fermentation is carried out by this particular organism is that the ferment is widely distributed in wine-growing countries, and that it grows especially freely in must, monopolising the nutrient matter and starving out other organisms. The fermentation is carried out in barrels for white wines—the bung hole being left open—and in open vats for red wines. Top fermentation and bottom fermentation are practised, as for beer. The former is the commoner, and is performed at a temperature of 15° to 25° C. = 59° to 77° F., the latter, chiefly used for Rhine wines, requiring a temperature not exceeding 15° C. = 60° F. A fairly high temperature—*e.g.*, 27° C. = 80° F.—favours the production of a wine in which the sugar is not completely converted, and which is, therefore, sweet and poor in alcohol, but with a good flavour. The main fermentation is complete in three to fourteen days, when the yeast falls to the bottom; the wine is then racked into clean casks. The "young wine" thus obtained undergoes a further fermentation, and as the percentage of alcohol increases, albuminous substances and tartrates are deposited—the latter being less soluble in alcohol than in

water—forming the crust known as "argol" (see *Tartaric acid*, Vol. II., Chap. XVIII.). When the marc is also allowed to ferment, the wine is highly coloured, owing to the extraction of the colouring matter of the skins by the alcohol. Such extractive matter helps to preserve the wine, on which account, and because of the presence of tannin, red wines usually keep better than white. Secondary fermentation in cask for wine on draught can be prevented by careful heating to a temperature of 55° to 60° C. = 131° to 140° F. in a separate apparatus, and storing in sterilised casks. Besides the alcohol produced by the fermentation of grape sugar, bye-products such as glycerin and succinic acid occur, similar to those formed from maltose in the manufacture of beer, and in addition to these, certain ethereal salts (esters) which impart to the wine its characteristic bouquet. The percentage of alcohol naturally present in wine is limited by the inhibiting effect which alcohol has upon the yeast. The usual quantity is from 6 to 12 per cent. Stronger wines are "fortified" by the addition of spirit. Besides these constituents, wine contains metallic salts of organic acids and extractive matter, including tannin and organic acids. Chemically, it is distinguished from beer by the presence of tartaric acid (which is characteristic of wine, as acetic acid is of beer), of a large proportion of salts, metallic and ethereal, and of tannin. At the same time it is devoid of bitter principles. The following table (*Fresenius* and *Borgmann*) shows the composition of some typical wines:—

	Grams per 100 c.c.		
	Hock.	Claret.	Moselle.
Alcohol, . . .	8·77	8·56	8·08
Extract, . . .	2·32	2·44	2·11
Mineral matter, . .	0·22	0·25	0·18
Acidity,* . . .	0·66	0·54	0·79
Glycerin, . . .	0·92	0·86	0·73
SO_3, ...	0·05	0·01	0·01
P_2O_5, ...	0·04	0·03	0·05

In pure natural wine the proportion of glycerin to alcohol is never less than 7·8 : 100. This serves as an index of the genuine character of the wine. The following are analyses (by *Dupré*) of "fortified" wines:—

* Presumably stated in terms of tartaric acid.

	Grams per 100 c.c.		
	Port.	Sherry.	Madeira.
Specific gravity, ...	0·9974	0·9979	0·9939
Alcohol, ...	17·53	17·20	17·75
Extract, ...	5·39	5·35	4·35
Glucose, ...	2·28	2·97	2·08
Mineral matter, ...	0·26	0·55	0·39
Acidity (tartaric acid), . . .	0·49	0·52	0·54
P_2O_5, ...	0·03	0·02	0·04

Alcohols higher in the series than ethyl alcohol are sometimes present in wine. The principal substance imparting the vinous bouquet is said to be œnanthic ether, but others are undoubtedly present, and each vintage appears to have its own characteristic ethers, said by some authorities to be due to the type of yeast used; some such flavouring matters are developed during storage. The colouring matter in white wines appears to be an oxidation product of the extractive matter in the juice. In red wines the colour is derived from the husks and seeds of the grape, and is only red in the presence of acid, being changed to green by alkali. Brown sherry is coloured with caramel (see *Sugar*, Vol. II., p. 182). Another change which takes place during storage is the deposition of some of the potassium bitartrate, together with colouring matter in the form of "crust," such as is seen in port. The addition of plaster of Paris to must hastens the fermentation, and is said to render the wine more stable, and to improve its colour. The chemical effect is to precipitate the tartaric acid as calcium tartrate, potassium bisulphate being formed. This reacts with the potassium phosphate present, forming free phosphoric acid and neutral potassium sulphate. It thus happens that a "plastered" wine is relatively richer in potash and phosphoric acid than one which has not been so treated. The practice is generally condemned.

Sparkling wines, such as champagne, are allowed to undergo a secondary fermentation in bottle. Thus, in the case of champagne, the racked new wine is mixed with old wine, and if there be not sufficient sugar to continue fermentation cane sugar or invert sugar is added immediately before bottling. The bottles are stored horizontally, and before being marketed are inclined until the sediment falls into the neck, when the cork is dexterously released, so that the pressure, due to dissolved CO_2, may expel the sediment.

IV. **MINOR FERMENTED LIQUORS.**—Besides beer and wine, other potable liquors containing alcohol are produced by the fermentation of saccharine matters, such as the juice of the

apple (for cider), and of the pear (for perry), and sugar itself (for ginger-beer). In making cider the apples are pulped, the juice is expressed and allowed to ferment spontaneously at a temperature of 4° C. = 40° F. The liquor is racked, and a secondary fermentation takes place at as low a temperature as possible. Good cider should contain from 5 to 6 per cent. of alcohol and 2 to 3 per cent. of sugar. Ginger-beer brewed from sugar by the action of the ginger-beer plant or of yeast, contains alcohol up to about 2 per cent.

V. **SPIRIT.**—The production of potable liquids containing alcohol dates from prehistoric times, but until chemical researches had been carried out by the alchemists and the process of distillation evolved, such liquids were not of greater strength than can be obtained directly by fermentation. When it was found that spirit of greater strength could be produced by distillation, the process became commercially valuable.

Raw Materials.—The earliest raw material used for the manufacture of spirit was wine. On distilling any ordinary wine, alcohol and water pass over, the former predominating in the first fractions, which are, therefore, richer in alcohol than was the wine. The distillation of wine for the production of spirit is still practised for the manufacture of the best brandy (cognac). When the rationale of fermentation became known, the fermentation of alcohol from sugar, both that naturally produced and that obtained from starch, was utilised for obtaining spirit. Thus, nowadays, wine, sugar, and starch are all used for the manufacture of spirit, the nature and flavour of the product depending mainly on the class of raw material adopted.

Potable spirits may be divided into two classes—viz., those produced by the distillation of materials which impart to them a characteristic and agreeable flavour, and those formed from materials which are treated to yield a spirit destitute of flavouring matter, and needing, therefore, to be artificially flavoured in order that it may be marketable. The former class was that originally manufactured (*e.g.*, brandy), the production of the latter class being a comparatively modern industry.

Brandy is the product of the distillation of wine; the best is known as **cognac**, from the place of that name, and is made from the brandy grape, a small white berry which yields a very acid juice, and is fermented for the express purpose of producing this spirit. Brandies from other districts are made from the wines from different grapes, each communicating a characteristic flavour to the spirit. The average yield is 10 to 15 per cent. of the wine employed. The following figures show the composition of a sample of cognac (specific gravity 0·93):—

	Per cent. (by weight).
Ethyl alcohol,	54·663
Normal propyl alcohol,	0·029
Isobutyl alcohol,	0·007
Amyl alcohol,	0·204
Furfural,	0·002
Wine oil,	0·008
Acetic acid,	Trace.
Butyric acid,	Trace.
Isobutyl glycol,	0·002
Glycerol,	0·005
Water,	45·080
	100·000

The colour of brandy is acquired from the cask in which it is stored, save in the case of brown brandy, which is coloured by the addition of caramel.

Whiskey.—The raw material used for the production of whiskey is barley, which may be entirely or partially malted; malted barley is used for Scotch whiskey, while for Irish whiskey a mixture of malted and unmalted grain is employed. The malting process is similar to that used by the brewer (see *Beer*, Vol. II., p. 191), the drying being effected over peat fires, which impart the characteristic smoky flavour to the whiskey. The dried malt is crushed and washed with hot water, as in a brewery, but under such circumstances as shall ensure the production of a wort containing more maltose and less dextrin than that intended for beer. The temperature employed is at first 160° F. = 71° C., and is raised until, at the third mashing, it reaches 185° F. = 85° C. The wort, when separated from the grains, has a specific gravity of 1·040. The spent grain, known as "draff," is similar in composition to brewers' grains, and is sold as cattle food; the composition of a sample is given by A. H. Allen (*Journal of the Society of Chemical Industry*, 1891, p. 305) as follows:—

	Per cent.
Moisture,	10·32
Oil,	6·70
Albuminoids,	19·88
Carbohydrates, digestible fibre, &c.,	41·06
Woody fibre,	19·00
Ash,	3·04
	100·00

The wort is cooled to 70° to 80° F. = 21° to 27° C. by refrigerators as quickly as possible, lest it become sour, and the fermentation is started at as low a temperature as is practicable, it being found that fewer bye-products (fusel oil) are then obtained. The boiling of the wort for sterilisation is omitted by the distiller

as the fermented liquor is only a stage in the process and is not stored. The surplus yeast of the brewer, in as pure a condition as possible, is used for the fermentation; impure yeast contains the acetic acid and other ferments, leading to loss of alcohol and production of aldehyde, an objectionable impurity. The fermentation is pushed as far as possible in a tun cooled by attemperators (see *Brewing*, Vol. II., p. 199), and the yeast is left in the fermented liquor or "wash," fresh yeast being required for each fermentation. The alcohol in the wash amounts to 10 to 12 per cent., and corresponds with about 80 per cent. of the saccharine matter employed.

The distillation of the wash is conducted in an ordinary still (pot still) of 6,000 to 12,000 gallons capacity, similar in shape to that used for distilling water in the laboratory, made of copper and fitted with an agitator to prevent the solid matter in the wash settling and charring on the bottom. The still is fired direct, and a small quantity of soap is sometimes introduced to prevent frothing. The distillate from this first still is poor in alcohol, and is known as "low wines;" the residue in the still ("pot-ale") contains 3 per cent. of solid matter in solution, including about 1 per cent. of lactic acid, which has lately been recovered and used as a substitute for acetic acid and tartaric acid in wool dyeing. The first distillate is redistilled in a second still similar to that just described, save that a stirrer is not necessary. The second distillate is collected in three fractions —namely, "fore-shots," "clean spirit," and "feints"; "spent lees" are left in the still and subsequently run to waste. The first and third fractions are impure, becoming milky on dilution with water, and are redistilled with the next batch of low wines. The middle fraction is "new whiskey," and has a strength of 13° to 50° over-proof (for an explanation of the term "proof," see below); it is brought to standard strength of 10° to 25° over-proof by the addition of water, and allowed to mature in cask.

The nature of the products of the fermentation of whiskey wash are similar to those of the fermentation of brewers' wort, but, as the process is carried farther, the formation of secondary products, particularly of alcohols higher in the series than ethyl alcohol, is greater. The impurities precipitated by water in the fore-shots, appear to consist largely of fatty acids (some of which may be derived from the soap used), but those precipitated from the feints consist chiefly of higher alcohols, which constitute the so-called fusel oil. The chief substance present in this body is inactive amyl alcohol, to which its evil odour may be attributed. With regard to the supposed injurious action of fusel oil on the system, Allen (*loc. cit.*) has shown that it may be freely imbibed without ill effect. The quantity present in whiskey is not greater than 0·1 per cent.; the ethyl alcohol present is usually 55 to 64 per cent., Irish whiskey being usually the stronger.

Besides these higher alcohols, furfural is present in whiskey, and is characteristic thereof; it appears to be produced by the slight charring of the solid matter in the wash. The maturing of whiskey appears to be due in part to oxidation, but more largely to an absorption by the wood of the cask analogous to that exerted by wood charcoal, in the purification of silent spirit (*q.v.*). The use of a sherry cask for storing whiskey is two-fold, impurities being absorbed from, and flavouring matters imparted to, the spirit.

Gin.—Whereas whiskey and genuine brandy are prepared in pot stills, in which but little fractionation takes place, gin—which is a liquor flavoured by the addition of flavouring materials to plain spirit in the process of rectification or redistillation—is manufactured in "patent" stills, such as are used for the production of pure alcohol. The raw material is a mixture of malted and unmalted grain, from which a mash is produced and fermented in the usual way (pp. 210, 211). The distillation is generally effected in a Coffey still, which is shown in Fig. 34. This apparatus consists of two columns, generally made of wood lined with copper. The first, A, is termed the **analyser**, while the second, B, is called the **rectifier**. The pipe C passes from the top of the analyser into the bottom of the rectifier. Internally the columns are divided by perforated copper plates (generally eleven in the analyser and fourteen in the rectifier), each of which is provided with two valves, having the appearance of the letter T in the figure. Each division of the column is connected to the next by a tube, D (a "dropping pipe"), which projects about 2 inches above the surface of the plate in which it is inserted, and terminates in a collar-shaped trap on the plate below it. The top of the rectifier is slightly modified, the fifth plate from the top being unperforated, but provided with a large opening, E, with a neck. The dropping pipe of this plate opens into a pan which is deeper than those under the dropping pipes of the other plates, and has a draw-off pipe, F. The upper divisions of the rectifier have the form of ordinary baffle plates. The whole of the upper portion of the column is the finished-spirit condenser. The wash (fermented mash) is stored in the vat, G, and flows into the well, H, from which it is forced by the pump, K, through the pipe, L, which passes through the rectifier; L is made up of a series of parallel portions connected with the bends, M, placed outside the rectifying column. The lower end of this pipe passes upwards to the top of the analyser, where the wash is delivered into the trap on the topmost plate, whence it flows from plate to plate, encountering steam from the boiler, N. The pressure of steam and alcohol vapour prevents the passage of the wash through the perforations of the plates, and compels it to fall from plate to plate through the dropping pipes. Surplus pressure is relieved by the valves in the plates. It will be

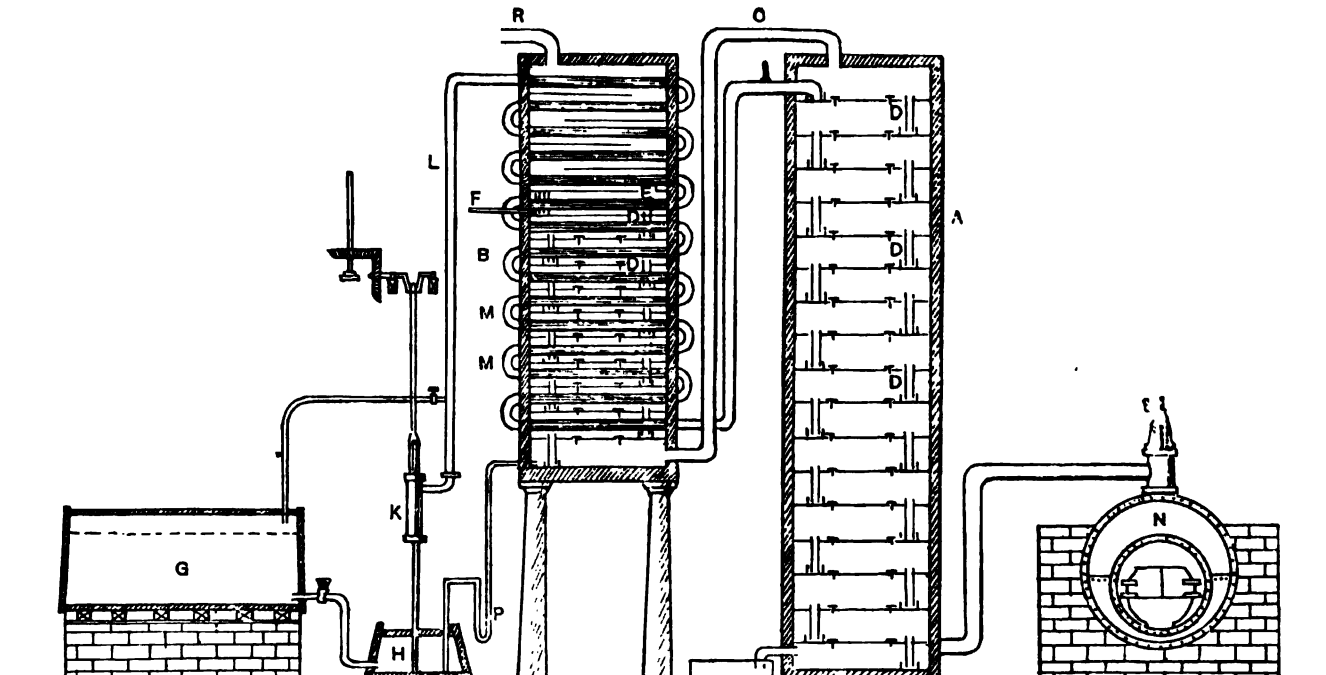


Fig. 34.—Coffey still.

A, Analyser; B, rectifier; C, pipe connecting A and B; D, dropping pipe; E, opening in plate; F, draw-off pipe for finished spirit; G, wash vat; H, well; K, pump; L, pipe passing through rectifier to analyser; M, connecting bends; N, boiler; P, pipe leading from the rectifier to the well; R, escape pipe.

understood that at the beginning of the process the apparatus has been completely filled with steam, so that the wash is heated nearly to boiling point before it enters the analyser. When the circulation has been started, the wash is continuously exposed in the analyser, in layers, to the action of the steam, which is at its lowest temperature at the top of the column, so that it is only from the top plate that the constituent of lowest boiling point (the alcohol) can pass away. It does so, together with the steam, through the pipe C, and is delivered at the bottom of the rectifier, during its passage up which it becomes concentrated by the condensation of the steam in contact with the pipes conveying the wash. The condensed steam, together with the impurities of higher boiling point (fusel oil), falls from the pipes on to the plates in the rectifier, and, by being thus delayed on its downward course, is deprived of the bulk of its alcohol. Lest the condensed water should still retain much alcohol, it is returned to the well, H, through the pipe P, to be again circulated with the wash. The concentrated and purified spirit comes in contact with the pipes conveying the coldest wash in the upper part of the rectifier, its cooling by this means being promoted by the presence of the baffle plates. The greater portion of it is thus condensed, and is ultimately collected as finished spirit through the pipe F. The more volatile impurities (*e.g.*, aldehyde) fail to be condensed in the rectifier, and pass away with such steam as remains uncondensed through the pipe R, and are either allowed to escape or are condensed and worked up again, according to the practice of the distiller. The spent wash flowing from the bottom of the analyser is used for heating the feed water of the boiler.

It will be seen that the Coffey still works much more systematically and economically than the ordinary pot still, inasmuch as the higher boiling constituents are continuously removed without redistillation in a second still, and the heat of condensation is utilised in warming the mash before distillation. On account of the perfect fractionation which is effected by the Coffey still, it is not adapted for the production of whiskey and similar spirits that depend for their flavour on the presence of characteristic impurities.

The plain spirit from the Coffey still is re-distilled in a pot still, such matters as are to impart flavour to the gin being added to the contents of the still. The substances chiefly used are angelica root, almond cake, calamus root, cardamoms, cassia, cinnamon, coriander, juniper, liquorice root, orris root and sweet fennel. These yield essential oils, which distil over with the spirit. The addition of salt to the contents of the still is found to favour the extraction of these flavouring matters. For the production of sweetened gin, syrup is added to the re-distilled spirit. It is sometimes customary to add a little sulphuric acid to the contents of the still, in which case fragrant ethers pass

over into the distillate. Such is the case with "Plymouth gin." "Hollands" differs from ordinary gin made in this country, in respect of the fact that it is made from rye and distilled from a pot still, its chief flavouring matter being juniper. The average strength of gin is about 17 to 22 per cent. under proof (37 to 40 per cent. of absolute alcohol by weight). It is often largely adulterated with water.

"**Absinthe**" is a form of gin flavoured with wormwood, as well as with the ingredients above-mentioned.

Rum.—Rum is imported from the West Indies—chiefly from Jamaica—where it is made for the most part from molasses (see *Sugar*, Vol. II., p. 164) or other refuse sugar. The fermentation is brought about by adding spent wash, to provide the necessary nutritive matter, to the sugar solution, containing 12 to 16 per cent. of sugar, and allowing spontaneous fermentation to ensue. The wash is then distilled in a form of pot still (the Pontifex still) until the bulk of the alcohol has come over, the "low wines" thus obtained being redistilled. Rum owes its flavour to the presence of ethyl formate and butyrate, and its colour to caramel, or to the extractive matter it takes up from the casks in which it is kept. Rum is usually 20° O.P.—*i.e.*, it contains 60·8 per cent. by weight of absolute alcohol.

Alcohol (*Commercial Spirit*).—Alcohol is prepared from many saccharine materials for industrial purposes, and for adulterating genuine potable spirits such as those described above. For the latter purpose, German spirit is largely used, made from potatoes, a somewhat cheaper source than the materials used in this country. Any starchy material will serve for the production of alcohol, and the real question is one of cost, which varies with the locality in which the manufacture is carried on. The saccharification of the starch is usually effected by the action of the diastase of malt, the quantity of malt requisite, according to German practice, being about 5 per cent. of the weight of potatoes used. It is reckoned that the work of saccharification is executed by half this quantity, the remainder serving as nutrient matter for the yeast in the subsequent fermentation. This extra nutrient matter is necessary on account of the small proportion of albuminous matter in potatoes and similar starchy materials. It is for this reason that the cheaper process of saccharification by boiling with a small quantity of acid (see *Starch sugar*, p. 181) is not a completely effective substitute for the use of malt. The method of mashing has been already described under the head *Whiskey*, Vol. II., p. 210; the "pitching" temperature is as low as is practicable (23° to 25° C. = 73° to 77° F.). The distillation of the wash is carried out in stills of the Coffey type, which produce alcohol containing 86 to 95 per cent. of absolute alcohol, and about 0·4 per cent. of higher alcohols, and similar impurities, collectively termed fusel oil. The kind of spirit

prepared from different raw materials is shown by the following figures:—

	Alcohol per cent. by weight.	Fusel oil per 100 parts absolute alcohol.
Potatoes, ...	89·04	0·328
,, ...	89·71	0·256
Turnips, ...	80·50	0·793
,, ...	78·10	0·818
Maize, ...	81·95	0·207
Molasses, ...	81·35	0·374

The raw spirit also contains some aldehyde, the presence of which is attributed to impurities in the yeast, which also cause the formation of higher alcohols. Aldehyde occurs more largely in spirit which has been fermented in warm weather than in that prepared under normal conditions of temperature. The value of this first distillate or "crude spirit" depends not only on its content of alcohol, but on the proportion of spirit free from impurities which it yields on redistillation. As already stated under *Whiskey*, it is generally supposed that fusel oil is objectionable in spirit which is to be used for drinking, but it is doubtful whether it can be condemned as actually deleterious, though its flavour is certainly nauseous. The spent wash is used as cattle food.

The crude spirit is purified by dilution with about an equal quantity of water—more water being needed the richer the spirit is in fusel oil—and filtration through wood charcoal, packed in columns varying in height from 7 to 30 feet, and about 3 feet in diameter. The wood charcoal, which is found to be more effective than animal charcoal, is used in pieces the size of peas or nuts, and acts partly by mechanical absorption, and partly chemically by inducing oxidation. As a consequence of this oxidation aldehyde and even acetic acid are formed. When the charcoal ceases to act, it can be revivified by steaming out the alcohol and igniting the charcoal with exclusion of air, but this latter treatment is not much practised, although the alcohol is always recovered.

The alcohol steamed out of the charcoal might be expected to contain a considerable proportion of the fusel oil that has been removed, it is found, however, that but little fusel oil is recovered, most of it being oxidised during the process of filtration.

The substitution of powerful oxidising agents—such as potassium permanganate, chromic acid, ozone and manganese dioxide—for charcoal has been proposed, but their use has not been attended with success, since they cause the production of much aldehyde and acetic acid, and, therefore, of ethyl acetate, from the ethyl alcohol. Of other methods which have been proposed may be mentioned that consisting in the extraction of the fusel oil by

treatment of the diluted crude spirit with petroleum ether, and that consisting in shaking the spirit with potassium carbonate, which forms a lower oily layer containing the higher alcohols and aldehydes; these, however, have not come into use.

The filtered spirit is then rectified in a column still. The following figures represent the output of a still of this kind, working on diluted and filtered crude potato spirit:—

	Per cent. by Volume.
First runnings (95 per cent. strength), ...	4
Second quality spirit (96·2 per cent. strength), . .	3
First quality ,, (96·4 per cent. strength), . .	37
Second quality ,, (96 per cent. strength), . .	0·5

The first runnings are too impure for drinking purposes, but are used for burning, for the preparation of vinegar (*v.i.*), and for such technical processes as the manufacture of mercuric fulminate (see *Explosives*, Chap. XVII.). The second quality contains 0·02 per cent. of fusel oil per 100 parts of absolute alcohol, and gives a perceptible aldehyde reaction. The better qualities contain no fusel oil, and only a trace of aldehyde. They constitute "silent" spirit, so-called because it affords no indication of its origin. The greater portion of this alcohol is flavoured for consumption, as brandy and other spirits, and is used for the fortification of wine. A smaller quantity is employed for pharmaceutical purposes and the manufacture of essences and scents. When "absolute" alcohol is required—*i.e.*, such as approaches in strength to 100 per cent. of alcohol—it is made by dehydrating the weaker spirit by means of quicklime, and redistillation.

The character of fusel oil depends to some extent on the material mashed, and on the method of manufacture—*e.g.*, the oil from grain or potatoes consists largely of the amyl alcohols—inactive amyl alcohol preponderating; that from the marc of brandy contains much normal propyl alcohol; that from beet contains iso-primary butyl alcohol as the predominating constituent. Fusel oil is but little used; its chief applications are as a solvent in chemical industries, as a source of the ethereal salts; thus it serves for the preparation of amyl acetate which is used for flavouring confectionery and as a solvent for celluloid (*q.v.*). A sample of fusel oil from potatoes had the following composition:—

	Per cent. by Volume.
Iso-propyl alcohol, ...	15·0
Propyl ,, ...	3·0
Normal butyl alcohol, ...	6·5
Iso-butyl ,, ...	5·0
Inactive amyl ,, ...	27·5
Active ,, ,, ...	6·0
Higher alcohols, ...	17·0
Ethyl alcohol, &c., ...	7·5
Water, ...	12·5
	100·0

Liqueurs.—These alcoholic liquids consist of "silent" spirit (*q.v.*) flavoured with various essences and containing much sugar. They are often artificially coloured. They contain from 40 to 50 per cent. of alcohol and from 25 to 50 per cent. of cane sugar.

Alcoholometry.—Inasmuch as the taxation of alcohol is a convenient source of revenue, much attention is paid to the strength of alcoholic liquors. The most usual method of ascertaining this value consists in taking the specific gravity of the alcoholic liquor or of the distillate from it, should it contain soluble non-volatile matter, which would affect the specific gravity. Pure alcohol has a specific gravity of 0·7938 at 15·5° C. = 60° F., and boils at 78·4° C. = 173·1° F. When mixed with water the volume of the mixture is less than the sum of those of the constituents, so that the specific gravity of mixtures are not calculable, and elaborate tables have been prepared empirically. The Excise system of stating alcoholic strength is in terms of degrees over or under "proof." Proof spirit was originally defined as of such strength that gunpowder moistened with it would just inflame when the alcohol was kindled. Now, it is defined to be a liquid of such a specific gravity at 51° F. that 13 volumes shall weigh the same as 12 volumes of water at the same temperature. Such alcohol has the specific gravity 0·91984 at 15·5° C. = 60° F., and contains 49·24 per cent. by weight of absolute alcohol (= 57·06 per cent. by volume). On this basis the term "under proof" means that the spirit contains so much water more than proof spirit per 100 measures, as is expressed in degrees below proof. Thus 20 U.P. means a spirit containing, at 60° F., 80 measures of proof spirit and 20 of water, and similarly 20° O.P. signifies a spirit of such strength that 100 measures, at 60° F., will be proof spirit when diluted with water to 120 measures. Absolute alcohol on this system is 75¼ O.P.

Methylated Spirit.—For the advantage of those who require alcohol for manufacturing purposes, a spirit is allowed to be sold free of duty, under certain restrictions, which is denatured by the addition of one part of wood naphtha to nine parts of rectified spirits of wine—*i.e.*, the strongest alcohol that can be obtained by ordinary distillation without a fractionating column. Rectified spirit has a specific gravity, at 60° F., of 0·838, and contains 84 per cent. by weight of alcohol. Wood naphtha (see *Destructive distillation*, Vol. II., p. 94) was chosen as interfering least with the industrial use of alcohol while rendering the spirit unpotable. Recently, however, it has been alleged that such methylated spirit is consumed as a beverage to the injury of the revenue, such consumption being possibly due to the greater purity of modern wood naphtha. In consequence of this, the use of spirit denatured with wood naphtha has been further restricted, and the bulk of methylated spirit as now sold is prepared by adding not less than ⅝ per cent. by volume of mineral

naphtha " of specific gravity not less than 0·800." This mixture is objected to by manufacturers as it becomes turbid on dilution, owing to the separation of the hydrocarbons constituting mineral naphtha. A different system obtains in Germany, duty-free spirit being there usually denatured by the addition of 2 per cent. of wood spirit rich in acetone and 0·5 per cent. of pyridine bases (see *Tar distillation*, Vol. II., p. 78). Industries for which such spirit cannot well be used are supplied with alcohol containing a constituent sufficiently nauseous to prevent the use of the spirit as a drink, but unobjectionable for the particular trade purpose. Thus spirit for varnish makers may be denatured by the addition of 0·5 per cent. of oil of turpentine.

VI. **VINEGAR.**—When wine, beer, or other alcoholic liquor containing nitrogenous matter is left exposed to the air, it soon becomes sour from the conversion of the alcohol into acetic acid. This change can be effected by oxygen in the presence of porous substances—*e.g.*, spongy platinum—the alcohol being oxidised according to the equation—

$$CH_3.CH_2.OH + O_2 = CH_3.COOH + HOH.$$

The oxidation of alcohol, however, in this manner is accompanied by the formation of aldehyde, CH_3COH, the lowest oxidation-product of alcohol. Moreover, vinegar is not merely dilute acetic acid, but contains as essential constituents aromatic and extractive matters. In practice, the oxidation of a dilute alcoholic liquor is effected by the agency of micro-organisms, chief among which are *Mycoderma aceti* and *Bacterium aceti*, the liquor being spontaneously infected by contact with the air. During the growth of this organism oxygen is absorbed and acetic acid produced, the mycoderma forming a skin (**mother of vinegar**) on the surface of the vinegar. It seems that the oxidation takes place without the intermediate formation of aldehyde, this occurring only when the mycoderma is losing its activity. Succinic acid appears to be formed in small quantity. In the course of time the organisms will oxidise the acetic acid itself to H_2O and CO_2. As in the case of other micro-organisms, it is essential that the nutrient liquid should contain mineral salts—viz., those of potash, magnesia, ammonia and phosphoric acid. The content of alcohol in the nutrient liquid should not much exceed 10 per cent., nor, for rapid growth, should it be less than 3 per cent. The most favourable temperature for the growth of the organism is about 30° C. = 81° F.

There are two main processes for making vinegar. In the one, the old Orleans process, which is practised chiefly in France, the access of air to the alcoholic liquid takes place solely by diffusion, so that the acetification takes a considerable time, and the process is known as the "slow vinegar process." In the other, a large surface of the liquid is exposed to the air, which is caused

to circulate over it, so that the process is completed in a far shorter time, on which account it is called the "quick vinegar process." Rapidity is only obtained at the cost of alcohol and vinegar, which are carried away by the circulating air, particularly if the temperature be allowed to rise unduly, as it may from the more rapid oxidation of the alcohol.

The slow vinegar process is used for making vinegar from wine, which should preferably be "full-bodied" and one year old. Vinegar from white wine is most esteemed. The wine is clarified by contact with beech shavings, and is then diluted if it contains more than 10 per cent. of alcohol, and run into casks of 50 to 100 gallons capacity, with holes for the admission of air, and placed on their sides on trestles. These casks have been previously one-third filled with strong boiling vinegar, in order to prevent them from flavouring the wine undergoing acetification. After eight days the wine is added in quantities of about 2 gallons, this quantity being again added at the end of every period of eight days until the cask is two-thirds full. Portions are drawn off to promote the circulation of air, and more wine is added as the process proceeds, the temperature being kept at about 25° C. = 77° F. by ventilation or artificial heating. The progress of the fermentation is judged by the periodical withdrawal of a sample from the top, a white froth indicating its completion; the process takes many weeks to carry out. It is usual to pass the vinegar through a rough filter, made of wood shavings or refuse from grape presses; this retains the *Mycoderma*, and completes the acetification of the alcohol. Upright tuns with false bottoms on which grape-press refuse is packed, are sometimes substituted for casks laid horizontally. In these the rate of manufacture is somewhat more rapid.

The quick vinegar process is adapted for the acetification of any appropriate alcoholic liquid, so that it is used in this country where vinegar is largely made from the alcoholic wash from a malt mash. Mashing and fermentation are conducted very much as in the process of brewing, save that the wort is well aërated in the fermenting vat, in order to induce more thorough fermentation, and the process is completed at a lower temperature, whereby the activity of foreign organisms is diminished. For the best production of vinegar the wash should be as bright as possible, and should, therefore, be allowed to settle and filtered before acetification.

Quick vinegar vats are wooden vessels, about 15 to 20 feet in height, 11 feet in diameter at the bottom and 8 feet at the top. The temperature of the vessel is regulated by a tin worm at the lower part, above which is a false bottom carrying a "filling" of beech wood shavings or twigs, which are previously steamed and soured with the vinegar. Above this, and below the lid of the vessel, is a revolving sparger of wood or ebonite, though other

methods of distributing the wort over the twigs are also in use. Perforations in the upper and lower part of the vessel serve for the circulation of air, which is slightly heated and regulated by closing the air holes above mentioned. The wash is pumped through the sparger and trickles over the filling, meeting the up-draught of air and having its alcohol oxidised to acetic acid by the action of the mycoderma, which collects on the twigs and shavings in the form of a slime; this growth necessitates the occasional cleansing of the apparatus. The oxidation of the alcohol is most satisfactory when the temperature due to the heat of the reaction rises to about 37° C. = 99° F. Too little air causes the production of the first product of oxidation of ethyl alcohol—aldehyde—which is very volatile and easily detected by its characteristic odour. Too much air is also to be avoided, as causing volatilisation of alcohol and acetic acid. In any case the loss of alcohol is considerable, averaging 12 per cent. of that contained in the wash. Complete acetification at one operation can be effected with liquors containing not more than 4 per cent. of alcohol, stronger solutions needing repeated treatment, with the addition of fresh raw material if a strong vinegar be required. Although vinegar containing as much as 12 per cent. of acetic acid can be thus produced, the strongest usually manufactured is of about half this strength. The manufacture of vinegar by this process takes from eight to twelve days. The air from the vats is sometimes passed through water to absorb the vapours of alcohol, aldehyde and acetic acid which it contains.

The manufacture of vinegar is usually conducted with little regard to those principles of fermentation by means of pure cultivations which have been worked out for beer brewing, the necessity for the presence of definite organisms, and for the exclusion of foreign germs by filtration of the air, being commonly ignored. Such diseases as the vinegar fly and vinegar eel are in consequence fairly common.

Vinegar has special characteristics, according to the raw material from which it is brewed. Thus, there are found on the market **cider vinegar**, **perry vinegar**, **ale vinegar**, and **sugar vinegar**, as well as the commoner varieties, **malt** and **wine vinegar**. Malt vinegar is brown and aromatic, owing this latter quality to the presence of ethereal salts, chiefly ethyl acetate, which is also sometimes added. The several qualities are designated by numbers, which express the number of grains of dry sodium carbonate which will neutralise 1 fluid ounce of the liquor. The specific gravity of malt vinegar varies from 1·021 to 1·025, and it contains from 3 to 6 per cent. of acetic acid, besides a little alcohol, and 5 to 6 per cent. of extractive matter. In order to preserve weak vinegar it is legally permissible to add 0·185 per cent. of sulphuric acid, but the practice is not adopted by manufacturers of repute. The expression "proof vinegar"

means vinegar containing 6 per cent. of acetic acid. Wine vinegar is pale yellow if made from white wine, and reddish-brown when made from red wine. It is more alcoholic than malt vinegar, and, therefore, has a lower specific gravity, 1·014 to 1·022; it contains from 6 to 12 per cent. of acetic acid. Potassium bitartrate, usually present to the extent of 0·25 per cent., is a characteristic constituent.

Malt vinegar is sometimes distilled, the product being known as white malt vinegar. Factitious vinegar is made from the acetic acid obtained by the destructive distillation of wood, diluted with water coloured with caramel and flavoured with ethyl acetate. The bulk of cheap vinegar sold in this country is of such nature. It does not contain the phosphates, tartrates, and nitrogenous matter characteristic of genuine vinegar.

CHAPTER X.

OILS, RESINS AND VARNISHES.

I. FATS, LIQUID AND SOLID.—All greasy substances of animal and vegetable origin may be classified as oils, including in the term solid oils (fats) and liquid oils (oils in the limited sense of the word). These substances are characterised by their unctuousness, by their insolubility in water, solubility in such solvents as ether, benzene and carbon bisulphide, and by their leaving a greasy stain on paper, which does not disappear by evaporation. Chemically, they are ethereal salts of the fatty acids; * the alcohol radicle of the salt is generally that of glycerin (glyceryl), but in certain waxes (liquid and solid) radicles of higher alcohols than glycerin occur. The misnomer **glyceride** is conventionally applied to fats of the former class. The number of fatty acids found in oils is large, but the chief occurring in oils of industrial importance may be given :—

General Formula.	Name.	Formula.	Melting Point.
$C_nH_{2n+1}COOH$	Butyric acid	C_3H_7COOH	−3° C. = 27° F.
	Valeric acid	C_4H_9COOH	
	Lauric acid	$C_{11}H_{23}COOH$	43·5° C. = 110° F.
	Palmitic acid	$C_{15}H_{31}COOH$	62° C. = 144° F.
	Stearic acid	$C_{17}H_{35}COOH$	70° C. = 158° F.
	Arachidic acid	$C_{19}H_{39}COOH$	75° C. = 167° F.
	Cerotic acid	$C_{26}H_{53}COOH$	81·5° C. = 179° F.
$C_nH_{2n-7}COOH$	Oleic acid	$C_{17}H_{33}COOH$	14° C. = 57° F.
	Dœglic acid	$C_{18}H_{35}COOH$	16° C. = 61° F.
	Erucic acid	$C_{21}H_{41}COOH$	34° C. = 93° F.
$C_nH_{2n-3}COOH$	Linoleic acid	$C_{17}H_{31}COOH$	
$C_nH_{2n-5}COOH$	Linolenic acid	$C_{17}H_{29}COOH$	
	Iso-linolenic acid	$C_{17}H_{29}COOH$	
$C_nH_{2n-3}(OH)COOH$	Ricinoleic acid	$C_{17}H_{32}(OH)COOH$	
	Iso-ricinoleic acid	$C_{17}H_{32}(OH)COOH$	
	Rapic acid	$C_{17}H_{32}(OH)COOH$	

The majority of solid fats consist largely of glyceryl stearate and palmitate.† The radicle glyceryl (C_3H_5) replaces 3 atoms

* Acids belonging to the fatty as distinct from the aromatic series, not necessarily homologues of acetic acid.

† The terms stearin, palmitin and olein are used as synonyms for glyceryl palmitate, stearate and oleate respectively.

of hydrogen, so that the formulæ for the above salts are $(C_{17}H_{35}COO)_3C_3H_5$ and $(C_{15}H_{31}COO)_3C_3H_5$. The predominant constituent in most liquid fats (oils) is glyceryl oleate, $(C_{17}H_{33}COO)_3C_3H_5$, while "drying" oils (*v.i.*) contain glyceryl salts of the acids of the linoleic and linolenic series. The specific gravity of oils and fats which have these substances as their chief constituents is lower than that of water, varying from 0·913 to 0·937.

The fats and oils have no boiling points, decomposition setting in when they are heated to 200° to 300° C. = 392° to 572° F. They cannot be distilled without decomposition, even under reduced pressure, in this respect contrasting with the fatty acids from which they are derived. Towards the higher limit of temperature given above, darkening generally occurs, carbon dioxide and much acrid vapour containing acrolein (C_2H_3COH) being evolved. On exposure to air and light, all oils and fats gradually suffer change. A distinction may be drawn between those which tend to "dry"—*i.e.*, to become converted by oxidation into solid resinous substances*—and those which do not exhibit this property ("non-drying oils"). The latter instead of drying become rancid. This change appears to be independent of bacterial action, and of that of unorganised ferments, and to need the conjoint influence of air and light. It results in the production of free fatty acids, generally poorer in carbon and richer in oxygen than are those characteristic of the fat, but the degree of rancidity, as implied by the nauseous smell and taste of the fat, has no direct relation with the percentage of free fatty acid. Nitrogenous substances, which are constant constituents of unrefined fats and oils, both animal and vegetable, appear to increase the rate at which rancidity develops. The breaking down of the fat into fatty acids as the main product must be accompanied by the decomposition of the glyceryl radicle, or the liberation of the glycerin corresponding therewith, but the exact fate of this constituent of the fat is at present unknown.

Like other ethereal salts, those of glyceryl are capable of conversion into the corresponding alcohol (glycerin), and an acid or salt of that acid. The term **hydrolysis** may be used to signify this change, however produced; true saponification (*v.i.*) is a particular case of hydrolysis. Thus, treatment with water at a high temperature resolves glyceryl palmitate in the following manner:—

$$\underset{\text{Glyceryl palmitate.}}{(C_{15}H_{31}COO)_3C_3H_5} + 3H_2O = \underset{\text{Glycerin.}}{C_3H_5(OH)_3} + 3\underset{\text{Palmitic acid.}}{C_{15}H_{31}COOH}.$$

This may also be effected by heating with sulphuric acid, the

* Compare the drying of linseed oil described below.

exact rationale of this change being scarcely understood, or by heating with a sufficiently powerful base, with which the liberated fatty acid will combine, the process being known as **saponification**, *e.g.* :—

$$\underset{\text{Glyceryl oleate.}}{(C_{17}H_{33}COO)_3C_3H_5} + 3NaOH = \underset{\text{Glycerin.}}{C_3H_5(OH)_3} + 3\underset{\text{Sodium oleate (soap).}}{C_{17}H_{33}COONa}$$

The group of fatty bodies known as **waxes** (the term including both liquid and solid substances) is sharply distinguished from ordinary fats and oils in that its members do not contain glyceryl, but are ethereal salts of alcohol radicles which only replace one atom of hydrogen (instead of three). Thus, beeswax contains the radicle of myricyl alcohol ($C_{30}H_{61}OH$), being myricyl palmitate, $C_{15}H_{31}COO(C_{30}H_{61})$. The waxes are generally more stable in air than are glyceryl derivatives, showing no tendency to dry or to become rancid. On hydrolysis, they yield their characteristic alcohols and acids in a manner similar to that of ordinary fats, though usually with somewhat greater difficulty.

Although several ethereal salts may be regarded as the predominant constituents of specified fats and oils, yet each individual fat or oil invariably contains two or more ethereal salts, similar in properties and differing but little in ultimate composition. The difficulty met with in attempting to separate the proximate constituents has given rise to the use of indirect methods of analysis and investigation, which although they do not in all cases determine accurately the nature and proportions of the constituents of any given oil, yet afford data sufficient for determining the identity of any given oil, and for giving an insight into its composition. Thus, the percentage of halogen (notably I and Br) which an oil will absorb under standard conditions, gives a measure of its content of ethereal salts of unsaturated fatty acids ; this value is termed the **iodine** or **bromine number** or **absorption**. Similarly, although it is impracticable to determine the molecular weight, or even the equivalent weight (because of the difficulty of complete proximate analysis), of the several constituents of an oil, with the view of ascertaining the nature of each ethereal salt present, yet a mean number for this value, characterising different classes of oils (*v.i.*), may be obtained from the percentage of base neutralised in the saponification of the oil. When this percentage is calculated in terms of an equivalent of the base, the mean equivalent weight of the oil is obtained. The mean equivalent weight of the oil is termed the **saponification equivalent.**

Thus, oils consisting chiefly of ethereal salts with a high equivalent weight have a high saponification equivalent, and those with a low equivalent weight a low saponification equivalent. Examples of each will be found below.

PREPARATION AND PROPERTIES OF THE CHIEF COMMERCIAL FATS AND OILS.—A convenient classification of the chief commercial fats and oils is that employed by Allen, which is based on a joint consideration of the origin, properties and constitution of the oils and fats classified.

(1) **Olive Oil Group.**—The members of this group are liquid vegetable oils containing glyceryl oleate as a principal constituent. They are non-drying oils, and are very liable to become rancid. Their specific gravity ranges from 0·914 to 0·920. Their halogen absorptions and saponification equivalents are moderate. Thus the iodine absorptions are from 80 to 100, and the saponification equivalents from 285 to 296. They show great tendency to solidify when exposed to nitrous acid, this solidification, characteristic of these oils, being known as the elaidin reaction, and probably consisting in a process of polymerisation which oleic acid and glyceryl oleate are capable of undergoing.

The chief members of this group are olive, almond, and earth-nut oil.

(2) **Rape Oil Group.**—These are liquid vegetable oils from the *Cruciferæ* containing glyceryl salts of acids of the oleic series, the most characteristic being brassic or erucic acid, $C_{21}H_{41}COOH$. The high equivalent weight of this acid gives these oils high saponification equivalents—*e.g.*, 315 to 330. Glyceryl salts of acids of the ricinoleic series are also present. These oils have a distinct drying tendency, indicating that they contain glyceryl salts of acids more unsaturated than those of oleic acid, a fact borne out by their comparatively high iodine absorptions—*e.g.*, 97 to 105. Their specific gravity ranges from 0·913 to 0·920; they form semi-solid elaidins. The chief representatives are rape oil and mustard oil.

(3) **Cotton Seed Oil Group.**—These are liquid vegetable oils ranging in specific gravity from 0·917 to 0·926. They all dry slowly and imperfectly, and are thus distinguished from the true drying oils. As might be expected from the fact that they dry, they have a fairly high iodine absorption (105 to 130), while their saponification equivalent is similar to that of oils of the first group. They yield semi-solid elaidins. The chief members are cotton seed, maize, sesame and sunflower oil. They probably contain glyceryl salts of acids of the linoleic and linolenic series.

(4) **Linseed Oil Group.**—These are the true drying oils; they are characterised by a high specific gravity, 0·924 to 0·938, and a high iodine absorption, ranging from 133 to 170. The saponification equivalent varies from 268 to 300. They contain glyceryl salts of unsaturated fatty acids, such as linoleic, linolenic and iso-linolenic acids, which are capable of oxidation and the production of varnish-like bodies (this change constituting the drying of the oil). The principal members are linseed, poppy-seed and walnut oils.

(5) **Castor Oil Group.**—These oils are distinguished by their great viscosity and high specific gravity (0·937 to 0·970).

Certain of these, notably castor oil, contain the glyceryl salt of ricinoleic acid as a characteristic constituent. The group is not otherwise possessed of distinctive qualities; the following oils are conveniently included here, as not falling into any of the preceding classes:—Castor, croton, curcas, and Chinese wood oil.

(6) **Palm Oil Group.**—These are vegetable oils solid at the ordinary temperature. Their characteristic constituents are the glyceryl salts of saturated fatty acids lower in the series than stearic acid—*e.g.*, palmitic acid. Their iodine absorptions (from the fact that saturated acids are mostly present) are low (34 to 54). Their saponification equivalents are also low (277 to 286). On account of these oils being solid at the ordinary temperature, their specific gravities at 15° C. = 59° F. are not comparable either among themselves or with those of other oils. The determination of the specific gravity of oils solid at the ordinary temperature, is generally made at 100° C. = 212° F., and comparison is then practicable. Thus, at this temperature the specific gravity of palm oil varies from 0·857 to 0·861. All these oils are liquid above 45° C. = 113° F. The chief members of the group are palm oil, cocoa butter and illipe oil.

(7) **Coco-nut Oil Group.**—These are also vegetable oils solid at the ordinary temperature. Their melting points are all below 30° C. = 86° F. They are characterised by containing the glyceryl salts of acids of the acetic series which are volatile with steam at 100° C. = 212° F.—*e.g.*, lauric acid. Their specific gravity at 100° C. varies from 0·868 to 0·878. The iodine absorption is generally low (7 to 15), and the saponification equivalent is also low (209 to 270). The chief members of the group are coco-nut oil, palm-nut oil and laurel oil. Two vegetable oils, somewhat analogous in respect of the fact that they are solid at the ordinary temperature, are Japan wax and myrtle wax, which are included for convenience in this group. They are not characterised, however, by the presence of glyceryl salts of the lower acids of the acetic series, Japan wax consisting mainly of glyceryl palmitate, and myrtle wax having a similar composition.

(8) **Lard Oil Group.**—These are animal oils, liquid at the ordinary temperature, and consisting chiefly of glyceryl oleate. They do not dry; their specific gravity at 15° C. = 59° F. varies from 0·914 to 0·916; their saponification equivalent from 290 to 299 and their iodine absorption from 55 to 75. The chief members of the group are neatsfoot oil, bone oil, lard oil and tallow oil, the last-named pair being expressed from lard and tallow respectively.

(9) **Tallow Group.**—These are animal oils, solid at the or-

dinary temperature. They are all liquid above 58° C. = 136° F. They consist essentially of glyceryl stearate, palmitate and oleate, the proportions of these bodies determining their consistency. Their specific gravity at 100° C. = 212° F. varies from 0·856 to 0·870, the latter figure being reached by butter fat, which is otherwise abnormal (*v.i.*). Their saponification equivalents (except that of butter) vary from 283 to 292; iodine absorption 33 to 62. The chief members of the group are beef and mutton tallow, lard, horse fat, bone fat and butter fat.

(10) **Whale Oil Group.**—These are marine animal oils containing glyceryl salts of fatty acids of the oleic series, although the drying tendency of many members lends probability to the belief in the presence of more easily oxidisable fatty acids; in this respect they resemble oils of the cotton seed group. Their specific gravity at 15° C. = 59° F. varies from 0·911 to 0·933; their saponification equivalent from 250 to 300, and iodine absorption from 99 to 166. Many oils of this group are distinguished by their content of the monohydric alcohol, cholesterol, $C_{26}H_{43}OH$,* occurring either in the free state, or as the salt of a fatty acid. The chief members are whale oil, seal oil, menhaden oil, cod-liver and shark-liver oil.

(11) **Sperm Oil Group.**—These oils (which are liquid at the ordinary temperature) do not contain glyceryl salts, but are essentially ethereal salts of such monohydric alcohols as dodecatyl alcohol, $C_{12}H_{25}OH$, and pentakaidecatyl alcohol, $C_{15}H_{31}OH$; the acids forming the salts are oleic and its homologue dœglic. The specific gravity of these oils is from 0·875 to 0·884 at 15° C. = 59° F. Their saponification equivalent varies from 380 to 456 and iodine absorption from 80 to 85. The chief members are sperm oil and dœgling or bottle-nose oil. These oils may be regarded as liquid waxes.

(12) **Wax Group.**—The members of this group do not contain glyceryl salts, and thus resemble those included in group (11), but are distinguished from them by being solid at the ordinary temperature. The principal salts contained in these waxes are cetyl and myricyl palmitates, and ceryl and myricyl cerotates. Their specific gravity at 100° C. = 212° F. ranges from 0·800 to 0·842. They are all liquid above 88° C. = 190° F. Their saponification equivalent is high, ranging from 438 to 900.

TYPICAL PROCESSES OF WINNING AND REFINING FATS AND OILS.

(1) **Methods of Winning and Refining Vegetable Oils.**—(*a*) **Oils from Seed and Fruit.**—The seed is either decorticated

* Both this body and an analogous substance, phytosterol, are found respectively in other animal and vegetable oils.

or not according to the quality of oil-cake to be produced, and crushed under stamps or between edge-runners or rollers. The crushed product is then submitted to pressure (generally in an hydraulic press), either cold, when a comparatively small yield of mild-flavoured oil is obtained,* or hot, when the maximum yield possible by pressure results. In the latter case the crushed seed passes from the rollers into a steam-heated kettle where it is sprinkled with water, the moist hot mass then going to the presses. The crude oil, containing debris from the seeds, dissolved resinous matter, colouring material, albuminous and pectinous substances and free fatty acid, is refined by subsidence, filtration through cloths, &c., by gravitation or pressure, and treatment with 1 to 2 per cent. of strong sulphuric acid (which chars albuminous matters), followed by alkali to decompose any sulphonic acids that may have been formed, and washing with water. After refining, oils may be improved in colour by filtration through animal charcoal, exposure to sunlight and treatment with oxidants—*e.g.*, potassium permanganate.

(*b*) **Vegetable Waxes.**—These are often rendered in the manner to be described for animal fats, or are extracted with a volatile solvent. If direct pressure be used, a higher temperature is requisite than is needed for ordinary seed oils, on account of the high solidifying point of vegetable waxes.

(2) **Methods of Winning and Refining Animal Oils.**—The process most generally in use is known as **rendering.** It is simpler than that necessary for the extraction of seed-oils, the reason being that much fat-containing material from animals is not only richer in oil than are seeds and the like, but also is enclosed in less impervious envelopes, animal membranes being less stable and mechanically resistant than are the cellulose husks and shells characteristic of vegetable oil-bearing materials. It is thus sufficient to boil the fatty matter with water or steam, and collect the oil which comes to the surface. In many cases, notably in winning marine animal oils, it suffices to allow the oil-bearing organ (*e.g.*, the liver) to soften by putrefaction, the oil draining out and the residue being rendered by moist heat. Purification is usually less elaborate than that requisite for seed-oils, and consists in rendering afresh with hot water or brine, or with dilute sulphuric acid.

(3) **General Method of Extraction by means of Volatile Solvents.**—The most rational method of winning oils when a maximum yield is the primary object to be obtained, is that used in the laboratory—viz., the repeated extraction of the oil-bearing materials with a volatile solvent, which is continually recovered by distillation and used again, the whole apparatus being typified by the well-known Soxhlet extractor. The

* The oil resulting from this process of extraction is known as "cold-drawn."

extraction, however, is liable to remove substances other than oil—*e.g.*, unsaponifiable matters of the class of cholesterol, and resinous substances. The process is, therefore, chiefly used for extracting residues from other methods of winning. The material is either extracted systematically in a series of steam-jacketed tanks or discontinuously in an apparatus similar to that shown in Fig. 35.

The material—*e.g.*, the residue from olive oil presses—is packed into the extractor, B, and carbon bisulphide is pumped from the tank, A, into the extractor, which it enters beneath the perforated false bottom, *d*. It percolates through the matter to be extracted, through the perforated plate d^1, and passes into the still, D, through the pipe shown at d^1. The carbon bisulphide, containing oil in solution, is distilled in D by closed steam, the

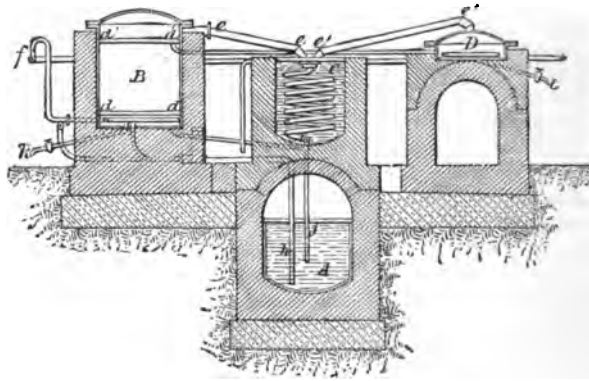


Fig. 35.—Oil extractor.

A, tank; B, extractor; *d*, perforated false bottom; d^1, perforated plate; D, still; C, worm; *k*, cock; *f*, steam pipe; *e*, pipe communicating with the worm, C; *l*, pipe leading from the still D.

vapour being condensed by the worm, C, and the liquid collecting in the tank, A. The process is continued until a sample of the solvent drawn from the cock, *k*, is found free from fatty matter. Steam is then injected under the false bottom of the extractor through the pipe, *f*, and the residual solvent thus distilled through the pipe, *e*—communicating with the same worm as that fitted to the still—into the tank, A. All the fat will ultimately remain in the still, D, whence it is drawn by the pipe, *l*. Carbon bisulphide is, in many respects, the best solvent for fats and oils, but its use is somewhat risky on account of its low boiling point (46° C. = 115° F.) and inflammability. Other solvents are used, notably benzene, ether, and light petroleum. Carbon tetrachloride has also been proposed, but its preparation is somewhat costly.

PROPERTIES AND USES OF THE CHIEF COMMERCIAL FATS AND OILS.—**Olive oil** is obtained from the fruit of several varieties of the *Olea Europæa*, the quality of the oil varying slightly with the class of tree yielding the fruit. The nearly ripe olives, containing 30 to 50 per cent. of oil, are generally first submitted to slight hand pressure, whereby the "virgin oil" is obtained. The yield of this is very small, the bulk of the oil being obtained by crushing the flesh in edge-runners or between rollers, followed by moderate pressure, the first product being the best. The **marc** or **press-cake** is broken up, stirred with boiling water, and then more strongly pressed; the second marc is similarly treated, the stones also being crushed and very strongly pressed. Each succeeding extraction yields an oil inferior to that preceding it; and the residual oil in the final press-cake may be obtained by extraction with volatile solvents. Inferior olive oil, not fit for dietetic purposes, but used for lubrication, although containing 7 to 8 per cent. of free oleic acid, is known as **gallipoli** or **engine oil**. Sometimes the kernels are crushed or extracted separately, yielding **olive kernel oil**, which is similar to low-grade olive oil. The yield of oil is some 20 to 40 per cent. of the weight of the fruit. Olive oil possesses the colour characteristic of the fruit, its green tinge being due to chlorophyll. It has a mild flavour when fresh, but becomes rancid more readily than true seed oils. It consists of about 70 per cent. of glyceryl salts liquid at the ordinary temperature (chiefly oleate), the remaining 30 per cent. being chiefly glyceryl salts of fatty acids of the acetic series (notably palmitic acid); these partially separate on cooling to about 10° C. = 50° F. The specific gravity of olive oil varies from 0·914 to 0·917 at 15° C. = 59° F., its saponification equivalent is 285 to 296, and iodine absorption 81·5 to 84·5. The oil is often adulterated with cheaper oils of about the same specific gravity, such as cotton-seed and sesame oil. It is used for eating, lubrication, burning, making Turkey-red oil (*q.v.*), and soap making.

Almond oil is obtained from both sweet and bitter almonds, but must not be confused with oil of bitter almonds (benzaldehyde). It much resembles olive oil, but is generally less coloured. It is used chiefly in pharmacy.

Earth-nut oil (arachis oil, ground-nut oil, pea-nut oil) is obtained from the fruit of *Arachis hypogæa* by drying and pressing, some 40 per cent. of oil being obtained as the gross yield of several treatments, 45 per cent. being about the content of the seeds. The cold-drawn oil is used for eating instead of olive oil, the remaining portions serving for lighting and soap making. The pressed oil cake, containing some 8 per cent. of oil, is used as cattle food. Earth-nut resembles olive oil in composition, save that a part of the glyceryl palmitate is replaced by glyceryl

arachidate, and part of the glyceryl oleate by glyceryl hypogæate. Arachidic acid has a melting point as high as 75° C. = 167° F., and its isolation and identification are used as a means of detecting and estimating the oil when present as an adulterant. The specific gravity varies from 0·916 to 0·920; saponification equivalent, 289; iodine absorption, 91 to 105.

Rape oil (*colza oil*) is obtained from varieties of *Brassica campestris*, the seeds being crushed, heated, and pressed in the manner described as characteristic of seed oils. The crude oil is refined by treatment with sulphuric acid, sometimes followed by alkali to remove traces of sulphuric acid and also free fatty acid resulting from the action of the sulphuric acid on the oil itself. The residual cake is used for manure. The oil-content of the seeds varies from 30 to 45 per cent., the yield from 28 to 36 per cent., and the quantity of oil left in the cake from 7 to 10 per cent. Rape oil contains glyceryl oleate and erucate, stearate and rapate. Its specific gravity is from 0·914 to 0·916 at 15° C. = 59° F.; saponification equivalent, 314 to 328; iodine absorption, 97 to 103. It is chiefly used for lighting and lubrication, and as an adulterant for olive oil. It is often adulterated with cotton-seed oil. Its viscosity is greater than that of any ordinary fatty oil, except castor oil, and is therefore taken as an arbitrary standard in viscosimetry. Rape oil becomes gummy on exposure to air, but does not actually dry.

Cotton-seed oil is expressed from the seeds of various species of *Gossypium* after the cotton itself has been removed. The seed and its cortex are cut through and parted by screening in a separator. The decorticated seed is then crushed for oil in the ordinary way. Decortication is particularly necessary for cotton seed, inasmuch as the oil cake left after expression of the oil is used for cattle feeding, a purpose for which it would be unfitted were the hulls suffered to remain. The content of oil in the decorticated seed is from 20 to 25 per cent.; the yield is about 15 to 20 per cent., and the oil cake retains about 10 per cent. The crude oil is dark in colour, and contains much pectinous matter. The colouring constituent is removed by treatment with alkali, and the alkali salt formed becomes blue on oxidation (**cotton-seed blue**). The specific gravity of refined cotton-seed oil varies from 0·922 to 0·924, its iodine absorption from 105 to 109, and saponification equivalent from 285 to 294. It has a slight tendency to dry, and is used as a substitute (admittedly or fraudulently) for olive oil in cooking, as a constituent of margarine, for soap making, and as an adulterant for most dearer oils and for making factitious lard. By freezing cotton-seed oil, the glyceryl salts, which are solid at low temperatures, are separated, constituting **cotton-seed stearin**, which is used as an ingredient of margarine. Cotton-seed oil consists chiefly of the glyceryl salts of oleic and linoleic acids, the drying properties of the oil being due to the latter.

Maize oil is contained chiefly in the germ of the grain, and is won by removing the germ previous to using the maize for spirit making, and pressing the separated germs in the ordinary manner. About 15 per cent. of oil is obtained, the residue constituting feeding cake. Maize oil is a yellow liquid of specific gravity 0·920 to 0·925, iodine absorption 116 to 122, and saponification equivalent of 280 to 290. The oil is used for lighting, lubrication and soap making.

Sesame oil is another example of the cotton-seed oil group. It is obtained by crushing the seeds of *Sesamum orientale*, commonly called *til-seed*. The seeds contain 47 to 56 per cent. of oil. The oil has a specific gravity of 0·921 to 0·924, an iodine absorption of 103 to 110, and a saponification equivalent of about 294. It is used as a food in place of olive oil, and is sometimes mixed with the latter as an adulterant; it is also employed for burning, lubricating and soap making. Sesame oil contains some 76 per cent. of glceryl oleate, the remainder containing glyceryl salts of acids of the acetic series.

The semi-drying properties of oils of the cotton-seed class are probably due to the presence of glyceryl salts of acids of the linoleic and linolenic series.

Linseed oil is by far the most important of the drying oils. It is obtained from the seed of the flax plant, which contains 30 to 35 per cent. of oil, the yield by pressing being about 26 per cent. The seed is crushed in the manner already described, and the oil cake used for cattle food. The oil is refined by treatment with a small quantity of sulphuric acid, with subsequent washing. Linseed oil, as obtained by simple pressure and refining, is known as **raw oil**, but when the oil has been heated to enhance its drying properties it is known as "**boiled oil**," and in that state is used as a vehicle for pigments. According to recent researches, linseed oil consists (disregarding the small quantity of glyceryl salts of acids of the acetic series solid at the ordinary temperature, which it contains) of some 65 per cent. of the glyceryl salt of iso-linolenic acid and 15 per cent. of that of linolenic acid, 15 per cent. of the glyceryl salt of linoleic acid, the remainder (5 per cent.) being glyceryl oleate. Linseed oil is generally yellow, but sometimes has a greenish tinge; its specific gravity varies from 0·930 to 0·937; iodine absorption 155 to 170; saponification equivalent 288 to 300. The characteristic property of linseed oil is that when spread in a thin film it dries to a varnish-like surface. The changes involved in this process are not fully understood. The oxidation of the oil involves the transformation of the acids named above into anhydrides of hydroxy-acids, one of which anhydrides is termed **linoxyn**. Glycerides of the hydroxy-acids themselves also exist in the dried oil. The precise composition of linoxyn is disputed, but it appears to be the chief constituent

of the film produced by the drying of linseed oil, and to owe its value largely to its insolubility in most menstrua. What has been said here with regard to linseed oil, applies also to other drying oils, which dry the more readily the more linolenic and iso-linolenic acids they contain. The quality of commercial linseed oil varies considerably, that known as Baltic being esteemed the best, while East Indian or Calcutta is inferior. Generally speaking, oil with a high specific gravity and iodine absorption is of better quality than that in which these analytical constants are low. Boiled linseed oil is prepared by heating the raw oil, either by a free flame or by high-pressure steam, to a temperature varying from 130° C. = 266° F. to 200° C. = 392° F. for several hours. Sometimes air is blown through the oil, and in all cases "driers" are added.* These bodies—types of which are litharge and manganous borate—probably act as carriers of oxygen. Only a small proportion of the drier added is dissolved by the oil. The drier is added to the extent of about 5 per cent. of the weight of the oil, and is first ground with oil to allow it to mix readily with the bulk. About 0·3 to 1·5 per cent. remains in the boiled oil produced. The process of boiling is probably one of polymerisation and limited oxidation; the appearance of ebullition is not due to true boiling, but to the escape of gaseous products of decomposition. Boiled linseed oil is darker than the raw oil, higher in specific gravity (0·937 to 0·952), and lower in its iodine absorption. It is frequently adulterated with rosin oil, which itself dries imperfectly.

When the boiling of linseed oil is pushed very far, a much larger amount of polymerisation and oxidation occurs, and the product is viscous, stringy, but not greasy, and forms the basis of printing ink. This process is conducted without the addition of driers, and is sometimes continued until the oil takes fire. Another product of the same type is the oil used for linoleum making. Most of this is prepared by exposing linseed oil already partly "boiled," but without appreciable darkening, to the air on sheets of textile material called "scrim" at a temperature of about 21° C. = 70° F. During this change much acrolein is evolved by the oxidation of the glyceryl radicle of the oil. The product, which is a tough translucent, gelatinous, non-greasy mass, is heavier than water; it is incorporated with cork powder and gum resins and formed into sheets. Recently, attempts have been made to expedite the oxidation by blowing air through the warm oil, instead of exposing it on scrim.

Blown oils are non-drying, or partially drying, oils, rendered very viscous by blowing air through the hot oil. They are used to impart viscosity to mineral lubricants. The change effected by blowing may be judged from the following figures for blown

* In the parlance of varnish-makers, a boiled oil is one which has been heated *after* the addition of driers. It is sometimes customary to add the driers to the heated oil after it has cooled.

rape oil:—Specific gravity at 15° C. = 59° F. 0·967, iodine number 63·6, saponification equivalent 280. Blowing with oxygen has also been suggested.

Castor oil is made from the seeds of *Ricinus communis*, of which there are two kinds, the small and large seeded. The former yields the better oil (used in medicine), and is cold pressed. The refining is performed by adding a pint of water to a gallon of the oil, and boiling until the water is evaporated and the mucilage deposited. The larger seeds are generally roasted, crushed, and boiled in water until the oil rises to the surface and can be collected. The seed contains about 55 per cent. of oil, 50 per cent. being about the yield obtained by several pressings. Castor-oil seeds contain a nitrogenous principle, ricin, of marked poisonous and purgative properties; the presence of a trace of this substance in the expressed oil probably imparts to it its well-known purgative property. Castor oil has a specific gravity at 15° C. = 59° F. of 0·958 to 0·970, a saponification equivalent of 309 to 319, an iodine absorption of 84 to 85. Its viscosity is very high—viz., 1,100, taking the viscosity of normal rape oil at 60° F. as 100. It is further characterised by its solubility in alcohol and sparing solubility in petroleum spirit. The characteristic constituent of castor oil is glyceryl ricinoleate, with which small quantities of the glyceryl salts of acids of the acetic series are associated. Castor oil, besides its use in medicine, is employed for burning, lubricating and soap making, and for making Turkey-red oil.

Turkey-Red Oil.—This is a generic title applied to the products of the action of sulphuric acid upon oils—*e.g.*, olive and cotton, but especially castor oil—which are used in mordanting fabrics to be dyed with alizarin. For making Turkey-red oil, sulphuric acid to the extent of from 15 to 40 per cent. of the weight of the oil is run into a vat containing the latter, in such a manner that the temperature can be readily controlled. After some twenty-four hours, brine is added as a washing agent. The use of brine is necessary, as the main product is soluble in water. A partial neutralisation with alkali follows, and water is added, so that the finished Turkey-red oil may contain some 45 to 50 per cent. of fatty matter. The action of sulphuric acid on the castor oil appears to result in the hydrolysis (p. 224) of the oil, and the formation of polyricinoleic acids and their sulphuric acid derivatives. The condensation of the ricinoleic acid (hydroxyoleic acid) may be typified by the following equations:—

(1) $HOC_{17}H_{32}COOH + H_2SO_4 = \underset{\text{Ricinoleic sulphuric acid.}}{HSO_4C_{17}H_{32}COOH} + H_2O$

(2) $HOC_{17}H_{32}COOH + HSO_4C_{17}H_{32}COOH = HOC_{17}H_{32}COOC_{17}H_{32}COOH + H_2SO_4$

"Diricinoleic acid."

About 65 per cent. of Turkey-red oil—*i.e.*, the sulphuric acid derivatives—is soluble in water, the insoluble portion consisting largely of unattacked oil and polyricinoleic acid.

Palm oil is expressed from the flesh of the fruit of *Elais guineensis*, a species of palm, after a period of fermentation. It has the consistency of butter, a yellow or reddish colour, and a pleasant smell. Its melting point varies from 25° to 36° C. = 77° to 97° F.; specific gravity at 15° C. = 59° F. is 0·920 to 0·927; saponification equivalent 277 to 286 and iodine absorption 48 to 54. It consists of glyceryl palmitate and oleate; it readily becomes rancid and frequently contains much free fatty acid—*e.g.*, 10 to 25 per cent. It is used for making axle-grease, soap and candles. The oil from the kernel of the same fruit (**palm kernel oil**) is also of buttery consistency, but contains a large proportion of glyceryl salts of lower fatty acids, and resembles coco-nut oil; it is used for soap making.

Coco-nut oil is obtained from the fruit of *Cocos nucifera*, the dried pulp (**coprah**), containing some 65 per cent. of oil, being shredded, fermented and pressed. It is refined by heating it with water until the latter has evaporated, as in the case of castor oil. The yield of oil is about 55 per cent.

Coco-nut oil is characterised by consisting chiefly of glyceryl laurate, some glyceryl salts of higher acids of the same series being present. It forms a white buttery mass, often containing a good deal of free fatty acid. When fresh its smell is agreeable and recalls its origin, but the oil easily becomes rancid. It melts at 20° to 28° C. = 68° to 82° F., its specific gravity at 100° C. = 212° F. is 0·868 to 0·874, and its saponification from 209 to 228; iodine absorption 7 to 9. The expressed cake is used for cattle food, and the oil for soap making (especially marine soap, Vol. II., Chapter XI.), nightlights, and as a constituent of margarine.

Neatsfoot oil is obtained from the feet of cattle, which are washed from blood, boiled, and the oil skimmed off; this forms an inferior grade; an oil of better quality is obtained by direct excision of fatty deposits. It is refined by subsidence, and then forms a yellowish oil, consisting mainly of glyceryl oleate, and therefore not readily becoming solid on cooling. Its specific gravity is 0·914 to 0·916 at 60° F. = 15·5° C.; saponification equivalent 299; iodine absorption 66 to 72. It does not easily become rancid, and is useful as a lubricant at low temperatures and for dressing leather.

Tallow is the generic name for the rendered fat of cattle and sheep. "**Mutton tallow**" includes the fat from sheep and goats; **beef tallow** that from neat cattle. The process of rendering consists in heating the crude fat by direct fire or closed steam, whereby the tissue is broken up and the fat separated. Dilute sulphuric acid is sometimes used for the same purpose of disintegrating the membrane enclosing the fat. The roasted tissues

from the open process are termed "graves," and are used for feeding pigs and poultry; the less heated tissues from the steam process are utilised for making ammonia and glue. The rendered tallow is refined by boiling with water and settling, and is often bleached by oxidising agents.*

Tallow consists essentially of glyceryl stearate (with some palmitate) and oleate, the former constituent amounting to from $\frac{1}{2}$ to $\frac{3}{4}$ of the whole. From this it is obvious that the analytical figures for tallow vary through a tolerably wide range. Thus, it melts at 40° to 45° C. = 104° to 113° F.; its specific gravity at 15° C. = 59° F. is 0·925 to 0·940, mutton tallow giving the higher value; saponification equivalent 283 to 290; iodine absorption 33 to 46, beef tallow having the higher value. When rancid, tallow often contains a good deal of free fatty acid. It is adulterated with bone fat and sometimes with cotton-seed stearin, as well as with non-fatty organic substances and mineral matter. It is used as a lubricant (Vol. I., p. 115) and for soap and candle making.

Lard was a term originally confined to the fat from the omentum of the pig, but is now applied to the whole fat of the animal. The parts containing fat are treated in a manner similar to that used in rendering tallow. Lard consists chiefly of glyceryl oleate and stearate, its softness depending on the proportions of these constituents. "Bladder lard," which is the best variety from the kidney fat of the animal, is hard and melts at 42° to 45° C. = 108° to 113° F. "Keg lard," an inferior quality, melts at 28° to 38° C. = 82° to 100° F. Lard is commonly adulterated by expressing lard oil from it and substituting the cheaper cotton-seed oil. (**Lard oil** is similar in its properties to neatsfoot oil, and is used for lighting and lubricating.) The specific gravity of lard at 100° C. = 212° F. is 0·859 to 0·860; saponification equivalent 280 to 292; iodine absorption 55 to 62. The chief use of lard is as a food stuff.

Butter is distinguished from all other fats by the large percentage of volatile fatty acids which it contains. Butter consists of the fat of milk (cream), agglomerated by breaking down the globules of which the fat is constituted. The collection of the cream is done by hand-skimming, or by the use of a centrifugal machine. Normal butter, not strongly salted, contains about 87 per cent. of butter-fat, 0·5 per cent. casein, 0·3 per cent. salt, and 11·7 per cent. water. Butter-fat itself consists of 60 per cent. of glyceryl oleate, 35 per cent. of stearate and palmitate, and 5 per cent. of butyrate, with traces of other low fatty acids of the acetic series. Butter, unless freed from casein, &c., or heavily salted, readily becomes rancid, its objectionable taste and smell, when in this condition, being due to butyric acid.

* Tallow is sometimes hardened by the conversion of its olein into elaidin by treatment with nitric acid (p. 226).

The specific gravity of butter-fat at 100° C. = 212° F. is 0·867 to 0·870; melting point 29° to 35° C. = 84° to 95° F.; saponification equivalent 241 to 253; iodine absorption 19 to 38.

Margarine is a substitute for butter, made by exposing beef or mutton suet, preferably the former, to a temperature of about 50° C. = 122° F., and collecting the liquid portion which drains away. This liquid is kept at 25° C. = 77° F. until the glyceryl salts, solid at that temperature, have separated, and the resulting mass is pressed. This last oil becomes buttery in consistency at the ordinary temperature. It is churned up with milk to give it a butter-like flavour. Should the product be too solid, it may be mixed with cotton seed oil; a yellow tint is imparted by annatto, turmeric or saffron. The main chemical difference between margarine and butter is the absence in the former of the glyceryl salts of lower fatty acids. (Coco-nut oil is sometimes used in making margarine, and supplies a certain amount of glyceryl salts of fairly low fatty acids. The characteristic flavour of coco-nut oil is removed by treatment with alcohol and animal charcoal.) The specific gravity of margarine is from 0·859 to 0·863; melting point 34° to 40° C. = 93° to 104° F.; saponification equivalent 285 to 290; iodine absorption 50 to 56.

Whale oil (*train oil*) is a typical marine animal oil obtained from the blubber of various kinds of whale by boiling this with water, and skimming off the oil. Glyceryl physetoleate, $(C_{15}H_{29}COO)_3C_3H_5$, and glyceryl salts of other acids of the oleic series, and of the acetic series, are the chief constituents of this oil. It is a brown liquid with a characteristic fishy odour. Specific gravity 0·920 to 0·931; saponification equivalent 250 to 296; iodine absorption about 110 or higher. Some marine oils dry rapidly. The chief uses of the oil are for soft soap making and leather dressing.

Cod-liver oil is prepared by washing and drying the livers, and putting them into open barrels; the oil slowly exudes, and is skimmed off the surface; it is filtered through blotting-paper to refine it. This product constitutes the best medicinal oil. The livers, after this treatment, are heated in sheet-iron pots suspended in boiling water, a further yield of oil being obtained. The older method is to throw the livers into a cask, and allow them to ferment, the resulting oil being ladled off as it rises. The residual livers are boiled in kettles until the water present is evaporated; the oil is strained, and, being crude and of a brown colour, is used only as tanners' oil. The therapeutic value of cod liver appears to be due rather to its easy assimilation as a fatty food, than to the minute quantity of iodine which it contains, that having been alleged to be useful. Cod-liver oil consists chiefly of glyceryl oleate and myristate, palmitate and stearate; a small percentage of glyceryl salts of volatile acids of

the acetic series is also present, and a small quantity of cholesterol. The specific gravity of cod-liver oil is from 0·925 to 0·930; saponification equivalent 263 to 303; iodine absorption 159 to 166. It is adulterated with other liver oils, and with seal oil.

Sperm oil is distinguished from all the foregoing oils by containing only small quantities of glyceryl salts. It consists essentially of dodecatyl oleate and physetoleate, and a little cetyl palmitate. It is obtained from the head of the sperm whale (*Physeter macrocephalus*) from which it is ladled out and drained away from the accompanying spermaceti. It is a yellow mobile oil not easily becoming rancid, and excellent as a lubricant. On account of its peculiar constitution its analytical constants differ notably from those of fatty oils consisting of glyceryl salts. Its specific gravity is 0·875 to 0·884; saponification equivalent 380 to 454; iodine absorption 81·3 to 85. The yield of higher monohydric alcohols obtained on its saponification is 38 to 41 per cent.

Spermaceti is the solid product associated with sperm oil. It consists essentially of cetyl palmitate. The crude material is of a yellowish colour, and is purified by being boiled with a limited amount of caustic potash, to saponify adhering oil. It has a characteristic crystalline structure; melts at 48° to 49° C. = 118° to 120° F.; specific gravity at 100° C. = 212° F. 0·808 to 0·812; saponification equivalent 438. It is liable to be adulterated with stearic and palmitic acids, tallow and paraffin wax. It is used in pharmacy and for candle making.

Beeswax is made from honeycomb, after the removal of the honey, by melting in water, allowing the impurities to settle and running off the wax. The yellow wax obtained in this way is often bleached by treatment with chromic acid, or exposure to sunlight, the bleaching being aided by the addition of a little fatty matter. Beeswax consists of about 80 to 85 per cent. of myricyl palmitate, the balance being chiefly free cerotic acid with a little melissic acid. Specific gravity at 100° C. = 212° F. is 0·819 to 0·829; melting point 62° to 64° C. = 144° to 147° F.; saponification equivalent 584 to 602. It yields 53 to 54 per cent. of myricyl alcohol on saponification. It is adulterated with water, mineral matter, foreign fats, paraffin wax and vegetable waxes. It is used for candle making and in pharmacy.

Bird lime may be mentioned here, as it is a substance standing between oils of the sperm oil class and the waxes. It is obtained as an extremely sticky tenacious mass by macerating the inner bark of the holly. It consists essentially of mochyl palmitate and ilicyl palmitate, both mochyl alcohol ($C_{26}H_{46}O$) and ilicyl alcohol ($C_{22}H_{38}O$) being monohydric.

II. TURPENTINES, RESINS, CAOUTCHOUC.

The resinous exudations from the stems of trees of the Coniferæ class consist of solutions of resins in essential oils, the most familiar example being common turpentine, from which rosin and oil of turpentine are obtained. The resins are compounds of carbon, hydrogen and oxygen, which have the character of acids or anhydrides, being capable of combination with alkalies. The essential oils are volatile hydrocarbons, usually terpenes of the general formula $(C_5H_8)_n$ and their congeners. Mixtures of hydrocarbons and resins of this type are also known as **oleo-resins.** When resins occur associated with gums instead of hydrocarbons, the mixed bodies are known as **gum resins,** while when benzoic acid and its congeners are present, the mixed bodies are called **balsams.**

Oil of Turpentine (*spirits of turpentine, "turpentine," "turps"*). The crude oleo-resin or true turpentine is an exudation from the barks of various conifers, and upon distillation, alone or with water, yields about 20 per cent. of oil of turpentine consisting of various true terpenes, $(C_5H_8)_2$. The oil of turpentine thus obtained may be rectified by addition of alkali to saturate resin acids, and redistillation. There are three commercial kinds of oil of turpentine. The American consists chiefly of **dextropinene.** Its specific gravity varies from 0·864 to 0·870 at 60° F. = 15° C., and it distils between 156° C. = 313° F. and 165° C. = 329° F. It usually contains a little resin in solution. The French variety is mostly **lævopinene,** but save for its direction of optical rotation is similar to American turpentine. Both are often adulterated with petroleum and rosin spirit.. They are used for making varnishes and as a vehicle for paints. On exposure to air they slowly resinify. Russian oil of turpentine has **sylvestrene** as its main constituent (66 per cent.), the remainder being dextropinene and cymene. It has a specific gravity of 0·862 to 0·872 at 15° C. = 60° F., and distils between 160° and 170° C. = 320° F. and 338° F. Russian turpentine is not available for paints and varnishes, for the resin which it leaves (2 to 5 per cent.) on evaporation, remains sticky. It is used for making "Sanitas" a disinfecting proprietary preparation made by blowing air through a mixture of the oil and water. The product appears to contain a peroxide of unknown constitution.

Essential oils.—Oil of turpentine, already described, is an example of one type of essential oils; several other classes exist. They are classified by Allen as **terpenes,** $C_{10}H_{16}$—*e.g.*, oil of turpentine and oil of lemon; **cedrenes** (sesquiterpenes), $C_{15}H_{24}$—*e.g.*, cedar oil; **aromatic aldehydes**—*e.g.*, oil of bitter almonds (benzaldehyde, C_6H_5COH); **ethereal salts**—*e.g.*, oil of wintergreen or methyl salicylate, $C_6H_4(OH)COOCH_3$. The chief methods of

winning these comprise extraction by pressure (as for oil of lemon); distillation in a current of steam, a generally applicable process, the oil when necessary being first liberated by fermentation (as for oil of bitter almonds); extraction with a fat or fixed oil, from which, if necessary, the essential oil can be removed by shaking with alcohol.

Oil of lemon is extracted by pressing the rind of the fruit just before ripening. Its chief constituent is a terpene, **limonene** (boiling point 176° C. = 349° F.). The specific gravity of oil of lemon at 60° F. = 15° C. is 0·870. It is used in confectionery and perfumery.

Cedar oil is prepared from red-cedar wood by the method of distillation. It consists largely of **cedrene**, $C_{15}H_{34}$ (boiling point 266° C. = 511° F.).

Oil of bitter almonds (benzaldehyde) is obtained by separating the fixed oil (p. 231) from bitter almonds by pressure, and distilling the residue with water; HCN and benzaldehyde, C_6H_5COH, are the products, being formed by the hydrolysis of the glucoside **amygdalin**, under the influence of an unorganised ferment **emulsin** which occurs in the almond. The oil is mixed with ferrous sulphate and lime, and redistilled, the hydrocyanic acid being thus fixed as calcium ferrocyanide. **Benzaldehyde** thus obtained is a colourless liquid boiling at 180° C. = 356° F., and having a specific gravity of 1·05. It can also be prepared synthetically from toluene, C_7H_8, by converting it into benzal chloride, $C_6H_5CHCl_2$, by chlorination, and heating the product with an alkali and water under pressure.

Oil of Wintergreen is obtained by distilling the leaves of *Gaultheria procumbens* with water; the yield is about 1 per cent. It consists essentially of methyl salicylate, often associated with a small quantity of terpene. Artificial methyl salicylate is prepared by distilling salicylic acid with methyl alcohol and strong sulphuric acid. It is a colourless liquid, specific gravity 1·18, boiling point 220° C. = 428° F. It is often adulterated with alcohol, chloroform and sassafras oil. It is used in medicine.

Many essential oils are associated with a class of bodies known as **camphors** or **stearoptenes**, of which common **camphor** ($C_{10}H_{16}O$) is a good type. Camphor is obtained by distillation of the wood of the camphor laurel with water, the crude product being purified by sublimation. It is a white crystalline solid, subliming without fusion at the temperature of the air. Specific gravity 0·986 to 0·996, melting point 175° C. = 346° F., boiling point 204° C. = 399° F. It is soluble in alcohol and sparingly soluble in water. It is largely used as a domestic insectifuge.

Resins.—Common rosin (*Colophony*) is—as already stated—the residue from the distillation of oil of turpentine from crude turpentine. American rosin has a darker colour than that from

European turpentine. White rosin owes its opacity to the presence of water. The specific gravity of common rosin varies from 1·04 to 1·10; rosin is soluble in most solvents except water; its melting point varies from 100° to 135° C. = 212° to 275° F., but it softens before melting. It consists essentially of abietic anhydride, $C_{44}H_{62}O_4$, easily transformed into the corresponding acid, $C_{44}H_{64}O_5$, by boiling with aqueous alcohol; its acid character causes it to dissolve in alkalies, and this solution has the properties of a soap, a fact utilised by employing rosin as an addition to fat in soap making (*q.v.*). Rosin has a saponification equivalent of 300 to 310, and a bromine absorption of 110 to 112. Rosin is also used for varnishes, and in soldering as a protective coating. Much rosin is also used for the manufacture of **rosin spirit** and **rosin oil** by destructive distillation. The former is the more volatile fraction. It amounts to about 3 per cent. of the rosin distilled. The quantity of the latter is about 85 per cent. of the rosin distilled; rosin oil is denser and has a higher boiling point than rosin spirit. Both consist of hydrocarbons of the olefine, acetylene and benzene series, with some terpenes and certain rosin acids. Rosin oil is a yellow or brown liquid, generally fluorescent, of specific gravity 0·98 to 1·10. It dries to some extent when exposed to air in a thin film, and unites with lime to form a grease (**rosin grease**) used in the manufacture of rough lubricants for trolley wheels. Rosin oil is used as an adulterant for many oils, especially boiled linseed oil, and also for making lithographic inks.

Copal is the rosin exuding from trees of the genus *Hymenæa* and others. Some specimens are soft and dissolve in ether, but good copal is hard and insoluble. It is light yellow or brown; specific gravity 1·06 to 1·08. On heating it undergoes change and becomes more soluble. It is chiefly used for varnishes.

Shellac is prepared from the crude rosin exuding consequent on the puncture of the tree *Ficus indica* by the insect *Coccus lacca*. The crude **stick-lac** is stripped off the twigs, and the **seed** or **grain lac** is melted in boiling water and poured on to a stone, when it breaks up on cooling into thin pieces. The aqueous solution on evaporation yields **lac dye**. For decolorising, bleaching with sulphurous acid or chlorine is adopted. Shellac is chiefly used for making varnishes, lacquers and sealing wax.

Gum benzoin may be taken as a type of the balsams. It is the exudation of *Styrax benzoin*. It contains from 10 to 20 per cent. of benzoic acid, the remainder consisting of resins. Its melting point varies from 85° to 95° C. = 185° to 203° F.

Peru balsam is a similar substance, containing cinnamic in place of benzoic acid. Its specific gravity is about 1·14.

Gamboge is an example of the class of gum resins as distinct from oleo-resins and balsams. It has a reddish-yellow colour and is composed of the resin **gambogic acid**, $C_{30}H_{35}O_6$ (64 to 74

per cent.), gum constituting the balance. It is used as a pigment, and, to a certain extent, in medicine.

Caoutchouc (*Indiarubber*).—This resinous substance is the inspissated sap of various genera of the three orders *Apocynaceæ*, *Artocarpaceæ*, and *Euphorbiaceæ*, trees which grow in tropical and sub-tropical countries. Trees of the two last-mentioned orders furnish the best caoutchouc, that from Para (in the Amazon district) being the variety of highest quality. Ceara in Rio Janeiro, Madagascar and Mozambique furnish inferior kinds. The sap of the tree is a milky emulsion, and is collected from incisions in the bark. It is coagulated by evaporation (spontaneous or artificial), or by the addition of acid or saline substances. An alkali (*e.g.*, ammonia) retains it in its liquid state. It is moulded into rough lumps or flask-shaped masses or films (Para rubber), for export. It is frequently very dirty, sticks and stones being added as intentional adulterants, and always contains albuminous matter and resinous substances. The imported rubber is cleansed by boiling it with water and macerating it between rollers over which a stream of water flows. The shredded and cleansed raw rubber is then incorporated with weighting and vulcanising materials (*v.i.*), and moulded into the form of the goods to be made. Commercial caoutchouc (rubber) varies much in composition, but its characteristic constituent is a hydrocarbon (a polyprene) of the formula $(C_5H_8)_n$. This is often associated with insoluble albuminous matter and from 1 per cent. upwards of resinous substances, these increasing in amount with the state of oxidation of the material. Common qualities contain much of this resinous matter. Pure rubber is serviceable for only a few purposes on account of its plastic and adhesive character, gently-warmed surfaces readily sticking together. When a strip of pure rubber sheeting is stretched to a comparatively slight extent, it returns slowly and imperfectly to its original dimensions. These properties serve to distinguish it from vulcanised rubber. When heated to 200° C. = 390° F., pure rubber becomes a sticky viscous mass, which is a product of decomposition, inasmuch as on cooling it does not harden to the consistency of the original rubber. When destructively distilled, it yields a mixture of hydrocarbons, including **caoutchene, isoprene, heveene**, all of the general formula $(C_5H_8)_n$. These products form an excellent solvent for rubber itself. Other solvents are chloroform, carbon disulphide, benzene and solvent naphtha, none of which, however, dissolves more than 5 per cent. of its weight of rubber. The utilisation of rubber depends on its remarkable behaviour with sulphur. When heated with 5 to 10 per cent. of sulphur to a temperature above the melting point of the sulphur, about 2 per cent. of the element (reckoned on the rubber) enters into some form of combination with the rubber. The product (**vulcanised rubber**) is

distinguished from raw rubber by its greater indifference to alterations of temperature—it neither becoming soft and sticky on moderate heating nor rigid on slight cooling—and by the possession of greater "elasticity" * and indifference to cold solvents, which, at most, cause it to swell, but do not take it into solution. The method of vulcanisation may be briefly described thus:—The raw rubber, being plastic, is capable both of being intimately mixed with the sulphur for its vulcanisation and with any mineral weighting materials that may be added, and of being moulded by any ordinary mechanical process—*e.g.*, rolling or squeezing through dies into sheet, cord, or tube form. The articles thus fashioned are kept in shape by appropriate moulds, which are heated, generally by high-pressure steam, to about 140° C. = 284° F., at which temperature the process of vulcanising takes place. Instead of sulphur, "golden sulphide of antimony" (Sb_2S_5) is sometimes used, which decomposes, affording sulphur for vulcanisation and becoming Sb_2S_3, thus imparting a red colour to the finished goods. Various loading materials—*e.g.*, chalk, zinc oxide, barium sulphate and lead oxide—are often added, especially to common goods. Lamp black is used for black goods. The vulcanising of rubber can also be performed by the use of sulphur chloride, S_2Cl_2, in dilute solution, CS_2 being the ordinary solvent. The solvent swells up the rubber and facilitates the penetration of the sulphur chloride. The process is largely used for waterproofing cloth and making thin rubber tubing; it cannot be used for thick goods, as the penetration is imperfect. But little is known of the nature of the action of sulphur in the dry process of vulcanisation, but the action of sulphur chloride has been studied by Weber, who is of opinion that the vulcanised rubber consists of two molecules of polyprene united by one or more double atoms of sulphur. The introduction of the sulphur is effected by the formation of polyprene sulphochlorides.

Ebonite or **vulcanite** is rubber vulcanised with so much sulphur (25 per cent.) that it is converted into a hard, horny mass quite different in appearance and mechanical properties from ordinary vulcanised rubber.

The deterioration of rubber goods appears to be a process of oxidation, resinous products being formed. Rubber is often largely adulterated with "surrogates" consisting of the products of the action of sulphur and sulphur chloride on oils—*e.g.*, rape and cotton-seed oil. These surrogates are gelatinous substances nearly devoid of mechanical strength, and are simply diluents of the rubber with which they are mixed. The use of these surrogates makes the determination of the specific gravity of rubber as a means of detecting adulteration altogether illusory. Common rubber goods made by moulding (called "mechanicals") are

* "Elasticity" is not here used in its exact mechanical sense.

also largely prepared from old vulcanised rubber re-worked. Indiarubber overshoes are examples of this class of rubber goods.

Gutta percha is a substance, similar in many respects to caoutchouc, obtained from *Isonandra gutta*, a tree found in the Malay Peninsula. It is collected in a manner similar to that used for caoutchouc. It has lately been proposed to extract gutta percha from the leaves of the tree by means of a volatile solvent. Like caoutchouc, gutta percha consists of a hydrocarbon associated with resinous matter. It is chiefly used as an insulating material in electrical work and for moulding purposes.

III. VARNISHES.

Varnishes may be divided into two broad classes, namely **oil** and **spirit varnishes**. The former class consists of those varnishes which contain a drying oil, capable itself of forming a varnish-like film when exposed to the air in a thin layer. The latter comprises those varnishes which are made up of some resin dissolved in a volatile solvent. The chief resins in use for varnish making have been already described; most of the other constituents of varnishes—*e.g.*, drying oils and volatile solvents—have been dealt with under appropriate headings; it remains to consider the methods of preparing varnishes, and such principles as are believed to underlie these methods.

(1) **Oil Varnishes.**—The typical constituents of an oil varnish are a resin—*e.g.*, copal; a drying oil—*e.g.*, linseed oil; and a volatile solvent—*e.g.*, spirits of turpentine. The first process in the manufacture usually consists in rendering the resin, or "gum," as it is technically termed, amenable to the solvent action of the oil. Many resins, prominent among which are copal, amber and animé, are almost insoluble in oil or spirits of turpentine, until they have been fused. Others, such as elemi and common rosin, can be dissolved without previous fusion. The operation of fusing or "running" is carried out by simply heating the resin in a large copper pot over a direct fire, the heating being continued until frothing from the escape of moisture or of gases from the decomposition of the resin, has ceased. Ordinary linseed oil of good quality is boiled in a manner similar to that adopted when boiled oil is the product sought (p. 234), and the two materials are then mixed, and heated together at about 500° F. = 260° C. for an hour or two, until the mixture becomes so viscous as to form strings, when a sample is drawn out for testing. The product thus obtained is thinned by the addition of spirits of turpentine, and the finished varnish is allowed to settle and run off into storage vessels. It appears that both the linseed oil intended for varnish making and the finished varnish

are improved by keeping, though the nature of the changes which they undergo is unknown. Specific directions as to constituents and quantities must be looked for in compilations of trade recipes. The process of drying which an oil varnish undergoes, takes place in two stages. In the first instance, the volatile solvent (spirits of turpentine) evaporates spontaneously, leaving a sticky film composed of the resin and drying oil, which have been used for making the varnish. The latter then dries by oxidation, and a film results, containing both the resin and the oxidised products of the drying oil. The quality of this film depends naturally both upon the nature of its materials, and the skill with which the varnish has been prepared. The resins must be chosen so that the film, though hard, is not brittle, but tough enough to resist a fair amount of wear and tear.

(2) **Spirit Varnishes.**—These are of the simplest description, merely consisting of solutions of any suitable resin in any appropriate volatile solvent. The resins most commonly employed are shellac, sandarac, elemi and mastic, and the commonest solvents are methylated spirit, spirits of turpentine and its various substitutes, and occasionally acetone. The method of preparation consists merely in warming the resin with its solvent, in a vessel heated by steam and provided with an agitator. It is fitted with a still head and worm, to recover any of the solvent which may distil over during the process of dissolution. The drying of spirit varnishes is simply the volatilisation of the solvent, the quality of the film left being dependent on the nature of the resins used. They are greatly inferior to oil varnishes in durability.

Recently, varnishes for special purposes, such as the slight or temporary protection of bright metal surfaces, have been made by dissolving the lower products of the nitration of cellulose (see *Explosives*, Vol. II., Chap. XVII.) in solvents such as alcohol-ether, amyl acetate or acetone.

CHAPTER XI.

SOAP AND CANDLES.

I. SOAP.—Soaps are the alkali salts of fatty and resin acids, soluble in water and capable of giving a lather. Inasmuch as they are made from vegetable and animal oils, they consist of the alkali salts of such acids as occur in these oils (see p. 223) together with those of the acids of common rosin (see p. 242). Caustic soda is generally employed in the process of soap making, usually yielding hard soaps, while caustic potash gives as a rule soft soaps. For the chemistry of the action of caustic alkalies on fats see p. 225. When free fatty acids are used for soap making, saponification can be effected by alkaline carbonates, which are also capable of acting on neutral fats at high temperatures, under pressure.

RAW MATERIALS.—The fatty matter most commonly used for good soap is tallow (palm oil and rosin being frequently added). A soda soap from this fat is hard and comparatively insoluble, but complete saponification without excess of alkali is difficult. Non-drying oils—*e.g.*, olive oil—also yield hard soda soaps. Semi-drying and drying oils—*e.g.*, rape, linseed, and fish oils—yield somewhat soft soda soaps, and are, therefore, generally used for making potash soap which is intentionally soft. Some oils containing lower fatty acids, notably coco-nut oil, are easily saponified, even in the cold, and nevertheless produce hard soaps. Waste fatty material from a large number of industries is generally worked up into soap, the product varying according to the character of the fat.

The description of the manufacture of caustic soda and potash is to be found elsewhere (see Vol. II., p. 30, and *Potash*, Vol. II., Chapter XVIII.). On account of the fact that saponification is generally conducted with a comparatively weak lye, the solution of caustic soda produced by the action of lime upon sodium carbonate solution suffices for the need of the soap maker, who therefore frequently makes his own lye. It is believed that the detergent property of soap is increased by the addition of certain alkaline substances, such as sodium silicate and aluminate. No such plea can be urged for inert mineral matter—*e.g.*, barium sulphate, kaolin and finely powdered pumice frequently used as filling for common soaps. Sodium sulphate is sometimes similarly

used in the manufacture of cold water soap, and water itself is often present in enormous proportion—*e.g.*, 60 to 70 per cent. Sugar is also used in making transparent soaps, and various colouring and scenting ingredients are employed, especially for toilet soap.

PROCESSES OF MANUFACTURE.—However the details of soap making may vary with the class of soap to be produced, the first part of the process merely consists in heating the fatty material and running in alkali of about 10 per cent. strength, little by little, so as to first emulsify the fat and then gradually saponify it, the completion of the process being judged by testing for the presence of free alkali. Salt is added to the contents of the copper containing the soap, and the soap is thus thrown out of solution, it being insoluble in brine. It rises to the top, and the brine, containing the glycerol of the fat freed by saponification, is run off. Fresh lye is then run in and the heating repeated, any residual fat being thus saponified, and the soap, which remains undissolved in the caustic liquor, being washed free from adhering salt. The subsequent treatment varies according to whether "curd," "mottled," or "fitted" soap is to be produced. For curd the soap is taken into solution again and allowed to rest until the dirt has settled; the surplus water is then evaporated, and the soap is run into frames where it solidifies. The separation of the lye is not quite complete in this process, so that the finished soap is somewhat alkaline, but contains less water than most other varieties.

Fitted soap is similarly treated, but is allowed a longer time for subsidence, and the boiling down is omitted. The finished product will obviously contain more water than curd soap, but be more nearly free from unsaturated alkali, the lye being given time to settle out. "Primrose" soap is the commonest example of a fitted soap, the raw materials saponified being about 7 parts of tallow and 1 of rosin. (Rosin soap alone cannot be precipitated with salt, but a mixed rosin and fatty soap is readily separated from its solution in this manner.) **Mottled soap**, if genuine, is manufactured similarly to curd, but is a second time boiled with lye until this has become strong enough to precipitate the soap again. It is then run directly into the frames after the surplus lye has settled. The frames are jacketed and the soap cools slowly, a circumstance which causes the total dirt of the materials to segregate in the lines which are last to solidify, producing a mottled appearance in the finished product. Since more than 20 per cent. of water prevents this segregation, by allowing too rapid subsidence of the impurities before the soap passes to the frames, mottling is generally regarded as an indication of freedom from excess of water. Seeing that now artificially mottled soaps are made in which the addition of sodium silicate solution is found to prevent subsidence even though much water

be present, this criterion of purity no longer holds good. Originally ferrous sulphide (from the crude alkali used) was the cause of the mottling; now manganese dioxide is used for artificially mottled soap. When it is desired to incorporate any particular scenting, colouring or disinfecting material, the soap is usually run into a "crutch-pan" (a tank with an agitator) on its way to the frames, and the selected ingredient here worked in. Fraudulently wet soaps may be externally hardened to conceal their true character, by exposing them in a steam closet to a temperature sufficient to dry the outer skin, the interior remaining wet. In soaps of the above-mentioned classes the process of manufacture involves the separation of the glycerin in the lye. Chemically it is practicable to recover this glycerin by precipitating the residual soap by the addition of lime, concentrating, fishing out the residual sodium chloride and distilling, but the cost of the process is usually too high to allow the product to compete with the glycerin obtained as a bye-product in candle making (*q.v.*).

Much soap is, however, made without separation of the glycerin. Thus, the oil or fat is gently heated (to about 45° C. = 113° F.) and mixed with warm lye. The mixture is covered and the saponification allowed to proceed slowly. The soap usually contains both free fat and free alkali. The addition of sugar solution produces a transparent soap; an excess of alkali is necessary in this case to ensure a good appearance. Soaps of this class are often sold for toilet use. **Soft soap** is also made without separation of glycerin, by saponifying drying and semi-drying vegetable oils and fish oils with caustic potash instead of soda. The greenish shade of much soft soap is due to the presence of hempseed oil, unless it be artificially communicated by the addition of ultramarine or indigo. The white specks sometimes present ("figging") are simply potassium stearate, and are no guarantee of good quality. **Toilet soaps** are made from best yellow soaps as a stock, and are mixed with perfume, &c., the process being known as "milling." The stock is cut into fine shavings, which are partially dried and are ground with the ingredients to be added. The paste is moulded into cakes by hydraulic pressure. Transparent soaps of good quality are made by completely drying the milled soap, dissolving in alcohol and distilling off the solvent, the transparency of the soap thus prepared being increased by the addition of syrup or glycerin. Common, much-advertised varieties of this class of soap have a nauseous smell, arising from the use of methylated spirit as a solvent in place of pure alcohol, and are moreover heavily loaded with sugar. Special "scouring" and "household" soaps often contain finely-divided sand or pumice powder up to 70 per cent. of the whole, whilst others are largely composed of carbonate of soda, the ground crystals or dry soda ash being used, and fancy

values assigned to the product. From a hygienic point of view, for personal use few soaps are so good as a common yellow fitted soap from a reputable maker.

The term soap is sometimes used to include the fatty acid salts of metals other than those of the alkalies. A typical soap of this class is "lead soap," or "lead plaster," made by heating lead oxide with olive oil and water, or by double decomposition of a lead salt and an alkali soap. It is a white waxy material used in pharmacy.

The cause of the detergent action of soap has been assigned to various reactions—*e.g.*, hydrolysis with the liberation of alkali, or with the production of a basic and an acid salt of the fatty acids present. The known power of soap to emulsify greasy material and to increase the brownian movement has doubtless much to do with the detergent action.

II. CANDLES.—The raw materials for candle making are (1) ethereal salts of fatty acids—*i.e.*, fats and waxes; (2) fatty acids prepared by the hydrolysis of fats; (3) hydrocarbons. The essential conditions to be fulfilled by a substance for candle making are, that it should be easily combustible, fairly fusible, and capable of burning without appreciably developing smoke or smell, when combustion is not aided by artificial draught. All these classes of candle-making materials are not equally efficient; thus glyceryl salts—*e.g.*, tallow—give a smoky and ill-smelling flame, from the incompleteness of their combustion; similarly, many hydrocarbons—*e.g.*, soft paraffin wax—become plastic at so low a temperature that the form of the candle is not retained while burning. A like objection applies to many free fatty acids. The function of the wick of a candle is to spread the combustible material over a sufficient area to allow of its rapid volatilisation by the heat of the combustion already proceeding. It is obvious that, inasmuch as this spreading is due to the capillarity of the wick, this quality must be adapted to the diameter of the candle (to maintain a fully melted cup of liquid fuel to supply sufficient combustible matter for the flame), and to the melting point of its material. In all candles but tallow dips, the wick is of plaited yarn, flat in form, and its burning end bends over, and protrudes through the side of the candle flame, so that it is consumed *pari passu* with the candle. In tallow dips, such a wick is inadmissible, because the very property which renders it serviceable in other cases—viz., its tendency to curve over—would shift it from the centre of a candle so plastic as is one made of tallow. Wicks for tallow dips are still made of twisted cotton, and require the use of snuffers.

Ceteris paribus, the higher the melting point of the material of the candle, the smaller the difficulty encountered in regulating the burning by an appropriate wick. The wicks are often treated

by steeping them in various salts—*e.g.*, phosphates and borates—which improve the burning, though the rationale of their action is by no means clear. The simplest method of candle making is that practised for **tallow dips**, which, as their name implies, are made by repeatedly dipping a bunch of cotton threads into molten tallow, and allowing the tallow to solidify on the wick between the dippings, the process being repeated until the candle is of sufficient diameter. On account of the complexity of the combustible, and of the impossibility of burning the wick uniformly with the candle, tallow candles give a nauseous smell when blown out, because the glowing wick destructively distils a portion of the fatty matter, acrolein, a highly irritating substance derived from the glyceryl, being probably a product. Pressed **coco-nut oil** (coco-nut "stearin") is used for making nightlights, though palmitic acid, tallow, "stearin" (not the acids, *v.i.*), and **paraffin wax** are also used. Another raw material which needs little preparation, and is applied very simply to the manufacture of candles, is **beeswax**, yielding, however, the highest grade of candles instead of the lowest, as does tallow. This superiority is based rather on cost than intrinsic merit. Wax is prepared by the candlemaker by shredding it, after it has been cleaned by washing it with hot dilute sulphuric acid, and exposing the shreds to light, whereby the wax is bleached; the bleaching is aided by the addition of a small quantity of fatty matter. Chemical bleaching with chromic acid, chlorine, &c., yields a wax less fitted for burning, as the granular character of the wax is accentuated, and if chlorine has been used, substitution products are formed which give off hydrochloric acid on burning. Owing to the fact that fused beeswax contracts greatly on solidification, wax candles are not cast but "poured," the process consisting in suspending the wicks on a frame, and pouring the melted wax down them until they have become of the requisite thickness. They are then rolled on a slab under a board to the required dimensions.

The variety of candle next in simplicity, in respect of its manufacture, to the foregoing classes is that made of **paraffin wax** (see Vol. II., pp. 102 and 121). The melted paraffin is poured at a temperature of about 180° F. = 82° C. into candle moulds surrounded by water at 200° F. = 93° C. The hot water is immediately drawn off and cold water substituted, in order that the candles may be rapidly chilled. The hot water is necessary to prevent the paraffin from setting on the outside immediately it flows into the mould, and the rapid cooling is essential to prevent the candles from sticking to the moulds. A candle-mould consists of a metal tube, of the shape of the candle, with the wick stretched along its axial line. These are arranged in sets with mechanical appliances for casting and withdrawing. Paraffin candles are translucent and nearly colourless.

Their quality varies with the melting point of the paraffin which ranges from 105° to 140° F. = 41° to 60° C. When the paraffin is of low fusing point, the candles gutter and burn wastefully, and easily bend in hot weather. A little stearic acid is sometimes mixed with the paraffin to improve the quality. **Ozokerite** (see Vol. II., p. 123) is also used in the same manner as paraffin wax. The manufacture of **sperm candles** from spermaceti is conducted in a manner similar to that employed for paraffin candles. They burn rather less irregularly than other candles, and are accordingly adopted as the Government standard of light. The preparation of fatty acids for the manufacture of candles constitutes an important chemical industry. Various means may be employed for the hydrolysis of the neutral fats and the obtainment of their fatty acids. The chief raw materials for the preparation of solid fatty acids for candle making are tallow and palm oil, any less solid fat giving too poor an output of fatty acids of high melting point. Hydrolysis of such fats may be effected either by saponification with a base or by the direct action of water or an acid. In the first case the saponification may be effected either in an open pan or under pressure. The base used is lime, of which 12 to 15 per cent. is required in the open pan process, and 2 to 4 per cent. when the operation is conducted under pressure. In the former instance saponification proceeds as in soap making by complete union of the lime with the fatty acids, and separation of the glycerin. In the latter, the quantity of lime is insufficient for saturation of the whole of the fatty acids, the base serving to initiate hydrolysis which is completed by the action of the steam. The open pan process consists in melting the fat in a lead-lined vat, running in milk of lime and agitating the mixture while steam is blown in. Calcium stearate, palmitate and oleate are formed, and glycerin is set free, the aqueous liquid containing it being drawn off and worked up for glycerin (*v.i.*). The solid lime salts, "rock," are boiled with dilute sulphuric acid, and the fatty acids thus liberated. These float to the top, and are skimmed off to be again boiled with very dilute sulphuric acid. The fatty acids are cast into flat cakes and these are submitted to hydraulic pressure, first cold and then at about 40° C. = 104° F. The liquid fatty acids, chiefly oleic acid, are thus expressed, and are sent into the market as "**red oil**" or "**olein**" used for soap making. The pressed cake of stearic and palmitic acids (so-called "**stearin**"*) is melted with very dilute sulphuric acid, in order to decompose any remaining lime salt. The purified "stearin" is cast into blocks with the addition of a little beeswax, vegetable wax or paraffin wax.

* The terms "stearin" and "olein," technically applied to the solid and liquid portions respectively of the fatty acids prepared for candle making, must not be confounded with the same words used to denote either the solid and liquid portions of neutral fats obtained by expression, or with glyceryl tristearate and glyceryl trioleate.

This treatment prevents the formation of visible crystals, and is known as "breaking the grain." The product is ready for casting into candles.

The method of hydrolysis with a limited amount of base under pressure is conducted in a stout copper vessel called an **autoclave**. In this the fat and lime or zinc oxide (2 to 3 per cent.) are mixed, and steam is blown in until the pressure rises to about 8 atmospheres (or higher if tallow be the fat undergoing hydrolysis). The product is treated for the separation of solid and liquid fatty acids in the manner described above for the pan process.

A process somewhat different in character from the foregoing consists in the hydrolysis of the fat by superheated steam, and the concurrent distillation of the products of hydrolysis—viz., fatty acids and glycerin. This is rendered possible by the influence of the steam in carrying over both fatty acids and glycerin at a lower temperature and with less decomposition than would be the case if steam were not used. In carrying out this process the fat is melted in a still, heated to 300° C. = 572° F., and superheated steam is blown in through a perforated pipe. The condensers consist of a series of vertical pipes, in the earlier members of which series the fatty acids for the most part condense, the more volatile glycerin collecting in the later members. Complete hydrolysis without breaking up of the desired products needs careful regulation of the temperature. Another method of hydrolysis is that in which the fat is treated at 150° to 177° C. = 302° to 350° F. with some 3 to 5 per cent. of strong sulphuric acid. After agitation and a period of rest, the fat will have been broken up, and other organic matters present will have been charred. The mass is then boiled with water and open steam, and the crude fatty acids are separated and heated to 116° C. = 241° F. to remove the remainder of the water, and distilled in a current of steam at a temperature a little below 300° C. = 572° F. A black tarry residue of "**stearin pitch**" (about 10 per cent.) is left in the retort, and is used as a substitute for asphalt and other bituminous materials in making black varnishes—*e.g.*, Japan black. The mixed fatty acids are pressed in the usual way, the liquid portion constituting **distilled oleic acid** in contradistinction to that won by saponification. The output by this process is somewhat higher in solid fatty acids (55 per cent. as against 45 per cent.) than that of the processes previously described. The reason for this is that a portion of the oleic acid is converted into iso-oleic acid (melting point 45° C. = 113° F.) by the action of the sulphuric acid. The manner in which the sulphuric acid acts, appears to consist in the liberation of the fatty acids with the formation from the glyceryl of a glyceryl sulphuric acid having the formula

$$SO_2\begin{cases} OH \\ OC_3H_5(OH)_2. \end{cases}$$

A portion of the glycerin is decomposed and lost. Some of the oleic acid (being unsaturated), combines with some of the sulphuric acid to form the compound,

$$C_{17}H_{34}\begin{cases}COOH\\OSO_2OH\end{cases}$$

which subsequently reacts with water to form hydroxystearic acid, $C_{17}H_{34}(OH)COOH$, and sulphuric acid. Hydroxystearic acid on distillation at a high temperature loses a molecule of water and polymerises to iso-oleic acid, $(C_{17}H_{33}COOH)_x$. Sulphuric acid is also used as a hydrolytic agent in a somewhat different way from that just described. The fat is mixed with about 4 per cent. of concentrated sulphuric acid, the temperature being about 100° C. = 212° F. The albuminous membranes of the fat are destroyed and incipient hydrolysis is induced. Water is now added and the hydrolysis completed by boiling the fat with the diluted acid which results. A treatment with oxidising agents—*e.g.*, a bichromate or permanganate, is necessary in order to cause the albuminous matters to settle. The free acids are washed and pressed in the usual fashion.

In all these processes the liquid fatty acids, amounting to about half the total fat treated, are less valuable than the solid fatty acids, and various plans have been devised for converting the former into solid products. Of these, the simple reaction of fusing oleic acid with caustic alkali—

$$C_{17}H_{33}COOH + 2NaOH = C_{15}H_{31}COONa + CH_3COONa + H_2$$

resulting in the production of sodium palmitate and acetate, has been used. The process, as originally carried out, was worked with the more costly caustic potash, because of the comparatively high fusing point of sodium palmitate, which led to overheating beyond the temperature proper to the reaction, and also on account of the poor conductivity of this salt, so that a uniform temperature could not be maintained throughout the mass. These drawbacks are met by the addition of some paraffin wax to the mixture of oleic acid and caustic soda. This ensures the perfect fluidity of the mass, and thus prevents overheating. The hydrogen is accompanied by hydrocarbons from the paraffin, and may be used as an illuminating gas. The process is carried on in a cast-iron cylinder with a sheet iron lid, through which the spindle of an agitator passes. Gentle heat is applied until the caustic soda (originally in aqueous solution) has dried, the steam escaping through a manhole. The vessel is then completely closed, save for a pipe to lead off the hydrogen, and the temperature raised to about 305° C. = 581° F. When the evolution of gas has ceased the mass is treated with water, and is thus separated into three layers—viz., a top layer of paraffin wax, a layer of sodium palmitate, and one of soda-lye containing sodium

acetate. The sodium palmitate is decomposed with sulphuric acid, and the palmitic acid distilled and used in the ordinary way. Other methods of obtaining solid fatty acids from crude oleic acid are (1) treatment with sulphuric acid, when iso-oleic acid is ultimately formed, as in the sulphuric acid process of hydrolysis (*v.s.*); (2) conversion into elaïdic acid (p. 226) by the polymerising action of nitrous acid, a process not applicable to impure oleic acid; and (3) conversion into solid products by the action of zinc chloride at 180° C. = 356° F., followed by washing with dilute hydrochloric acid, then with water, and distillation in a current of steam; the solid part of the distillate consists chiefly (75 per cent.) of stearolactone,

$$C_{14}H_{29}CHCH_2CH_2$$
$$\quad\quad\quad\quad\quad\quad |\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad O \text{ —— } CO$$

together with some iso-oleic acid.

The manufacture of candles from the solid fatty acids prepared by any of these processes is effected in the moulds previously described, warm water being used to surround the moulds, the exact temperature required depending on the tendency of the acid to crystallise. Stearic acid candles crack if chilled (in casting) too suddenly, and crystallise if cooled too slowly.

Glycerin is obtained as a bye-product in the saponification and hydrolysis of fats in soap and candle making. As already stated (see *Soap*), difficulty is experienced in recovering glycerin from spent lyes, on account of their dilution and the impurities which they contain. The process of recovery consists essentially in precipitating residual soap with milk of lime, evaporation to crystallise as much of the sodium chloride as possible, neutralisation with acid to precipitate albuminous matter, precipitation of remaining traces of fatty matter as the salt of a metal such as iron, copper or aluminium, and a second evaporation whereby more sodium chloride is separated. This crude glycerin contains about 80 per cent. of $C_3H_5(OH)_3$, and contains salt, and compounds of sulphur and arsenic (the last named from the sulphuric acid). Refined glycerin, free from mineral matter, is prepared by distilling the crude product with superheated steam (at 210° C. = 410° F.), the distillate being collected in a series of vertical condensing pipes, the first one or two of which are not artificially cooled, so that glycerin condenses almost alone, the steam and remainder of the glycerin being collected in later members of the series, which are jacketed with water. The distilled glycerin is decolorised by animal charcoal which has been freed from soluble salts by washing in hydrochloric acid. Finally, concentration is effected in a vacuum pan. Another method of separating the salt from the glycerin is by dialysis, as in the diffusion process for the manu-

facture of sugar (see Vol. II., p. 166). The recovery of glycerin from "sweet-water," which is the aqueous solution obtained from the saponification of fats with lime or zinc oxide for candle making, is a simple process, inasmuch as there is no salt to be removed. Mere evaporation is, therefore, sufficient to obtain a fairly pure glycerin. This is effectively conducted by means of an apparatus consisting of a trough containing the glycerin to be concentrated, into which paddles, heated internally by steam, dip, so that by the revolution of the shaft carrying the paddles, these latter are periodically exposed, coated with glycerin, to the air, and the water is thus driven off from the films of glycerin on the paddles at a low temperature. The process can be improved by enclosing the whole apparatus in a vacuum vessel. Owing to the volatility of concentrated glycerin, even at a temperature—*e.g.*, 100° C. = 212° F. —much below its boiling point, 290° C. = 554° F., weak glycerin cannot be concentrated beyond a strength of 70 to 80 per cent. by boiling in the air without incurring serious loss; hence the devices described above. It has been proposed to concentrate aqueous glycerin by freezing it, when the portion which solidifies contains more water than the rest of the liquid; freezing has also been applied to the purification of crude concentrated glycerin, in which case the glycerin solidifies (at 20° C. = 68° F.), the solidification being aided by the addition of a crystal of glycerin. Glycerin is a sweet colourless liquid, specific gravity 1·262, of great viscosity, and miscible in all proportions with water and alcohol. It dissolves many substances—*e.g.*, metallic salts—which are soluble in water. It takes fire at 150° C. = 302° F., and burns with a blue flame. It is most largely used now for the manufacture of nitro-glycerin (see Vol. II., Chap. XVII.). Minor uses are in pharmacy, soap making, filling instruments which require a liquid seal and are exposed to low temperatures—*e.g.*, wet-gas meters *—and sweetening wine.

*Mixtures of glycerin and water have lower freezing points than has either constituent.

CHAPTER XII.

TEXTILES AND BLEACHING.

I. TEXTILE FIBRES.—For the production of a textile fabric some material of parallel longitudinal structure and considerable tensile strength is requisite. Typical substances possessed of these properties are the animal and vegetable fibres—*e.g.*, wool and cotton—and inorganic fibres, such as asbestos and slag wool (see *Iron*, Vol. I., p. 133).

(1) **WOOL.**—Wool is an epidermal appendage similar to hair, but differing from it in that it lends itself better to textile pur-

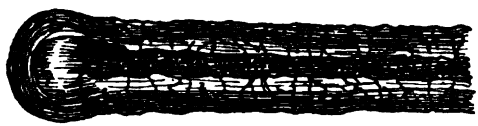


Fig. 36.—Hair.

Fig. 37.—Wool.

poses on account of its greater elasticity and its more loosely adhering scales, which cause it to felt together more readily. The difference in the structure of wool and hair is shown in Figs. 36 and 37.

It will be seen that there is no difference in the internal structure, but that the scales of the wool fibre are attached to the stem for a shorter portion of their length than are those of the hair fibre. As the scales of such fibres interlock when brought into contact, it is possible to spin the individual fibres into a coherent thread. "Diseased" wool will not interlock in this manner, from the imperfection of the scales. The mechanical and chemical treatment of wool, previous to spinning, has chiefly for its object the cleansing and opening out of its scales. The length of the individual fibres of wool (known as its "staple") varies from 1 inch to 1 foot, or even more.

The characteristic constituent of hair and wool fibre is a nitrogenous body termed **Keratin**, which appears to be identical with

the substance existing in horn. The average composition of wool fibre is—

	Per cent.
Carbon,	49·25
Hydrogen,	7·57
Oxygen,	23·66
Nitrogen,	15·86
Sulphur,	3·66

Raw wool consists of wool fibre associated with wool fat, **wool** sweat (suint), water and dirt (known collectively as "yolk"); its composition varies between wide limits.

The hygroscopic character of wool is, to a certain extent, dependent upon its percentage of fat; the greater the amount of fat, the smaller the quantity of moisture. In consequence of this, wool should always be bought and sold on its analysis. Raw wool has to be freed from suint and fat before it can be spun. For this purpose it is washed, several methods being in use. Ordinarily the washing liquid is water, supplemented by weak soap solution, but volatile solvents, such as petroleum spirit and carbon disulphide, have also been proposed. In the washing both wool fat and suint are removed, and may be recovered from the wash water by precipitation with sulphuric acid, the product being known as **wool grease**. Wool fat is not a true fat, but consists of the alcohols **cholesterol** and **iso-cholesterol**, and the oleates and stearates of these bodies.

Crude wool grease is used for the manufacture of **lanolin**, the form in which cholesterol is commercially used as an unguent. The grease consists of cholesterol (about 70 per cent.) and fatty acids (30 per cent.), precipitated by sulphuric acid from the potash salts present in the unwashed wool and from the soap used in washing it. By treatment with caustic soda these acids are dissolved and an emulsion is formed, from which, on dilution, crude lanolin separates. Lanolin owes its therapeutical value largely to the fact that, unlike fats, it readily emulsifies with water and is rapidly absorbed by the skin. The substance commercially known as **Yorkshire grease** is the total fatty matter recovered from the water used for wool washing, and from that used to cleanse the wool from the oils employed as lubricants in spinning. Hence, besides fatty acids, neutral fats and cholesterol, it may contain mineral oil, should the latter have been used for lubricating the wool. Where the wool fat is not worked up for lanolin, potash is recovered from the potassium salts of fatty acids present in the true sweat (suint), which is the portion of the "yolk" soluble in water (see *Potash salts*, Vol. II., Chapter XVIII.). The presence of potassium salts, tending to form soaps, in wool grease doubtless aids the emulsification of neutral fats, and the property which cholesterol possesses of emulsifying with water has a similar influence. These facts explain the efficacy of water for cleansing wool.

Cleansed wool fibre has a specific gravity of 1·30; it is not easily acted on by dilute organic or mineral acids, but is attacked by even dilute alkalies, especially when hot, being in these respects similar to other animal fibres (*e.g.*, silk), and distinguished from vegetable fibres, such as cotton, which are more readily affected by acids than by alkalis (*v.i.*).

(2) **SILK** is the secretion of the caterpillar *Bombyx mori* used in the formation of the cocoon in which it envelopes itself previous to passing into its chrysalis condition. Silk fibre being a glutinous secretion, dried in the form of a thread, has no characteristic structure like that of wool, but consists merely of a core of the nitrogenous body **fibroin** (corresponding in composition with the formula $C_{15}H_{23}N_5O_6$), surrounded by a coating of **silk glue**, another nitrogenous substance called **sericin** ($C_{15}H_{25}N_5O_8$), which is partly soluble in hot water to a gelatinous solution. Mulder gives the following analysis of Neapolitan raw silk :—

	Per cent.
Fibroin,	53·4
Gelatin,	20·9
Wax, resin and fat,	1·5
Colouring matter,	0·05
Albumin,	24·4

It is probable, however, that the substance recorded as albumin is an alteration product of fibroin, the percentage of which is therefore greater than that given above. As in practice, the loss by "boiling off" (*q.v.*) is from 25 to 30 per cent., the amount of residual matter reckoned as fibroin may be put down as 70 to 75 per cent. In winding raw silk from the cocoon, the silk glue is only softened and not dissolved. Complete removal of the silk glue can be effected by boiling, and is necessary in certain stages of treatment of silk, which are described later. The behaviour of silk fibre to reagents is as follows:—It is weakened by prolonged boiling with water, but to a smaller extent than wool (*Knecht*). It is also less attacked by alkalies than is wool, the reverse being the case with regard to acids. It cannot be successfully bleached by chlorine as it is attacked thereby, and is accordingly treated with milder bleaching agents, such as soap. Various "wild" silks are used to a considerable extent, that from the caterpillar *Antheræa mylitta*, constituting **tussur silk**. Unlike silk from the silk worm, tussur silk is not formed of a single thread from which the whole cocoon is spun, but of several discontinuous threads, on which account it is less easy to spin. Its fibre is larger and more elastic than that of ordinary silk. It is more highly coloured, and has to be bleached by hydrogen peroxide.

Silk fibre is very hygroscopic, and should be sold on its analysis. Its specific gravity is about 1·33. **Artificial silk** has been prepared by forcing solutions of nitrated cellulose in alcohol,

ether, acetic acid and similar solvents, through capillary tubes, so that it issues in a fine stream which passes through water and parts with its solvent, becoming coherent and elastic like natural silk. The inflammability of the material is reduced by denitration, effected by treatment with alkaline sulphide solutions, and the thread is spun in the usual manner. The manufacture is not yet a commercial success.

(3) **COTTON** is the fibre surrounding the seeds of plants of the genus *Gossypium*, several varieties of which yield commercial cotton. The cotton fibre (Fig. 38) consists of a tube of irregular shape, having walls composed of approximately pure cellulose. It is seen in a nearly pure state as unspun but cleansed cotton (cotton wool). Its composition is given as follows (*Hugo Müller*):—

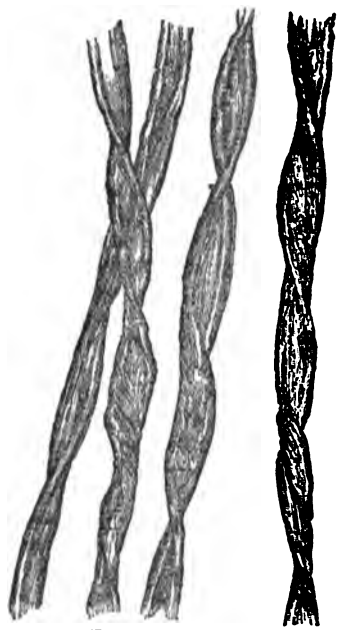


Fig. 38.—Cotton.

	Per cent.
Cellulose, . . .	91·35
Moisture, . . .	7·00
Wax, ...	0·40
Aqueous extract, . .	0·50
Ash, ...	0·12
	99·37

The commercial quality of cotton is determined by the uniformity of diameter and the length of "staple" of the fibre, the former varying from 0·0004 to 0·001 inch, and the latter from 0·77 to 1·80 inch. It is but little attacked by dilute acids in the cold, but at higher temperatures, or by stronger acids, it is acted upon, becoming disintegrated. It is only slightly attacked by long boiling with dilute alkalies in absence of air, but when air is present it becomes converted into oxycellulose (see *Mercerising*). Being nearly pure cellulose it behaves like this compound towards strong acids (see *Nitrocellulose*, Vol. II., Chap. XVII.). It can be bleached by chloride of lime without undergoing appreciable deterioration.

(4) **FLAX** is the bast fibre of various species of plants of the genus *Linum*, the most important being *Linum usitatissimum*. After removing the seeds from the stems by a combing process termed "rippling," the flax stems are "retted" in order to separate the bast fibres from each other and from the true wood of the stem. "Retting" consists in submitting the stems to the

action of water until they begin to rot. This process is performed either in stagnant water or in a running stream. A mere exposure to dew for many weeks, or treatment with tepid water, steam or mineral acids, may be substituted. When water alone is used, fermentation speedily sets in which effects the disintegration of the cementing material (pectose) of the fibres. When hot water, steam or acids are used, a species of hydrolysis effects the same end, the pectose being converted into pectin, which is soluble in water, and into pectic acid, less readily soluble. Mechanical processes known as "breaking," "scutching," and "heckling," which are beating and combing processes, complete the isolation of the flax fibres. Raw flax fibre has the composition :—

	Per cent.
Cellulose,	81·99
Wax,	2·37
Matter soluble in water,	3·62
Moisture,	8·60
Ash,	0·70
Pectous substances,	2·72
	100·00

Flax essentially differs from cotton in that it consists of separate cells, disposed longitudinally along the fibre, with cross septa. The cell-walls are very thick, and the internal cell space very small. The "staple" of flax varies from 2 to 3 feet, and the ultimate fibres vary in length from 1 to 1½ inches, and in width from 0·006 to 0·010 inch, and are pointed at their ends. Flax is colder to the touch than cotton, being a better conductor of heat, as its air spaces are smaller than those of the cotton fibre. It is stronger than cotton, and, being invested with pectous substances, is more resistant to reagents, and requires somewhat more drastic treatment to bleach it (*v.i.*). The colour of flax varies according to the nature of the retting to which it has been subjected, such as has been treated in stagnant water being much darker than that retted in running water.

(5) **HEMP** is the bast fibre of a variety of plants, chief among which is *Cannabis sativa*. The fibre is freed from incrusting substances by processes similar to those described under flax. It resembles flax fibre, but has a higher tensile strength (30 to 35 as compared with 20 to 25 kilos. per sq. mm.), and resists the retting action of water better, on which account it is used for ropemaking and similar purposes.

Raw hemp fibre has the composition given below :—

Cellulose,	77·13	per cent.
Wax,	0·55	,,
Aqueous extract,	3·45	,,
Moisture,	8·80	,,
Ash,	0·82	,,
Pectous substances,	9·25	,,
	100·00	,,

(6) **JUTE** is the bast fibre of various species of *Corchorus*. The staple of jute varies from 6 to 12 feet, but the ultimate fibres are very short (about $\frac{1}{12}$ to $\frac{1}{8}$ inch), on which account it is weaker than flax or hemp, and proportionately less valuable. The cells constituting the ultimate fibres are more lignified than those of flax, and, in the opinion of Cross and Bevan, consist chiefly of a body termed ligno-cellulose, containing 75 per cent. of true cellulose, and 25 per cent. of lignin, into which constituents it is decomposed by treatment with acids and alkalies. Raw jute fibre has the following composition:—

Cellulose,	63·76 per cent.
Wax,	0·38 ,,
Aqueous extract,	1·00 ,,
Moisture,	9·86 ,,
Ash,	0·68 ,,
Pectous substances,	24·32 ,,
	100·00 ,,

Various other bast fibres, notably **China grass**, are employed as textile raw materials. Other fibrous plants, such as grasses (*e.g.*, **esparto**), are used for rough textile fabrics, but find their chief employment in papermaking, under which head they will be considered.

(7) **WOOD-WOOL** is prepared by cutting thin boards into strips and digesting them with sulphurous acid, as in the bisulphite process for making wood pulp (see *Paper*, Vol. II., Chapter XIV.). The boiled wood is partially dried and passed through corrugated rollers, and may then be separated into coarse fibres. For finer fibres, the pulp must be completely dried, and combed, after pressing, by methods similar to those employed for flax. It is used as an absorbent for surgical dressings. **Tow** is the broken or waste fibre produced in the various mechanical processes for preparing flax and similar textile fibres for spinning.

(8) **MINERAL FIBRES.**—The most important of these is **asbestos**, which is the name given to various natural silicates which are fibrous in structure. The name thus relates rather to physical condition than chemical composition, as may be seen from the following analyses:—

	Italian.	Canadian.	Scotch.
SiO_2,	40·30	40·57	56·15
MgO,	43·37	41·50	22·46
CaO,	...	...	11·72
FeO,	0·87	2·87	3·11
Al_2O_3 and Fe_2O_3,	2·27	0·90	1·93
H_2O,	13·72	13·55	2·50

Typical Italian and Canadian asbestos is therefore essentially an hydrated silicate of magnesia, while other less valuable kinds are of irregular composition, indicated by the third analysis. Before the fibre can be woven it has to be separated, as the mineral occurs massive. The fact that true asbestos contains combined water causes it to undergo change when heated to redness, the water being driven off and the fibre much impaired, although fabrics made of it are sufficiently fireproof to retain their form and remain fairly coherent.

Slag wool is another mineral fibre, and is made by allowing jets of steam to impinge on a stream of molten blast furnace slag (see *Iron*, Vol. I., p. 133), whereby the slag is divided into threads, generally laden with globules of slag which have failed to be prolonged into fibres. It is used chiefly as a fireproof and non-conducting lagging material.

Glass wool is merely glass softened over the lamp and drawn out into long threads, which are capable of being spun into fabrics. Except as a laboratory requisite it is curious rather than useful.

II. BLEACHING.—The treatment of textile fibres by the numerous processes included under the term bleaching, has for its primary object the removal of natural colouring matters, and of such impurities as would cause uneven dyeing, or would play the part of mordants, fixing the dye in places where it is not required. In general, the treatment comprises processes for cleansing the fibre, so as to expose it to the action of the bleaching agent, and for oxidising or reducing those natural colouring matters, which are still retained, to colourless products.

Thus, it happens that all the processes may be classed under the heads (1) cleansing or scouring, and (2) bleaching, however many operations each stage may involve. Since, during the spinning and weaving of textile goods, the fibre always becomes contaminated with oily and other matters—either accidentally, or designedly for the purpose of lubricating or strengthening the fibre—this matter must be removed by the scouring process, as well as any natural fatty, waxy or resinous matter which may have remained after treatment of the raw fibre. The method is, therefore, essentially a saponification process, and alkalies are used for the purpose. It will be gathered, however, from what has already been said in this chapter concerning the resistance of fibres to chemical change, that those of animal origin must be more tenderly treated than the vegetable fibres, and that the same statement holds with regard to the second or bleaching process. It is for these reasons that, although the chemical principles underlying the scouring and the bleaching of textile fibres are the same for all fibres, involving saponification and oxidation or reduction, as indicated above, yet the details of the processes, and to some extent the agents employed, vary

according to the nature of the fibre. In what follows, an outline of the essential processes adopted for each particular fibre is given.

Wool Bleaching.—The scouring of the raw wool has already been discussed (p. 258). During the process of spinning and weaving, the wool is treated with oily lubricants, such as olive oil, oleic acid and mineral oil, which facilitate the movement of the fibres by counteracting the tendency of the scales to interlock (p. 257). These lubricants must be removed before bleaching can be effected, by immersing the hanks of yarn or pieces of cloth (wool being bleached in both forms), in a solution of soap, ammonium carbonate (the active constituent of the stale urine formerly employed) or sodium carbonate, at a temperature of 35° to 45° C. = 95° to 113° F. Volatile solvents have been to a slight extent substituted for these feeble alkalies (p. 258). After washing, the yarn is ready for dyeing or bleaching.

Bleaching is accomplished by exposing the wool to sulphur dioxide generated from burning sulphur. The common process is known as "stoving," and is carried out in a brick chamber lined with wood, on the floor of which the sulphur is burned. The sulphur dioxide may also be applied in solution, into which the wool is dipped; or solution of sodium bisulphite or sodium hyposulphite may be used. It appears that the chemical change involved in the bleaching, be it reduction or mere combination with the sulphur dioxide, is not a very deep-seated one; for treatment of the bleached wool with alkaline substances, such as soap, restores the yellow colour of the unbleached wool. Any sulphur dioxide which may be mechanically retained can be removed by immersion in dilute hydrogen peroxide.

The colouring matter may also be bleached by oxidation, by soaking the wool in slightly ammoniacal hydrogen peroxide at about 35° C. = 95° F. for some hours. Recently, a solution of sodium peroxide has been substituted for the ammoniacal hydrogen peroxide; magnesium sulphate may be added to neutralise the alkalinity of the sodium compound, and the goods may subsequently receive a wash in a dilute acid bath to generate hydrogen peroxide from the sodium peroxide. The bleaching obtained by hydrogen peroxide or sodium peroxide is permanent.

The use of bleaching powder solution for decolorising wool is impracticable, because the treatment is too drastic, rendering the wool harsh and brittle; moreover, chlorinated wool has a yellowish tint. For woollen fabrics which are to be printed, it is recommended to pass the stoved goods through a chloride of lime bath, since the chlorination of the wool aids the mordanting of the colour.

SILK BLEACHING.—The appearance and texture of raw silk are greatly improved by removing the sericin (p. 259) before

weaving. This is the object of the process known as "discharging," "ungumming," or "stripping." When "boiled-off" silk—*i.e.*, silk nearly completely freed from silk-glue—is required, the hanks of silk are immersed in a soap bath at a temperature of 90° to 95° C. = 194° to 203° F. A transference to a second and third bath is advisable after a short time, lest the colouring matter accumulating in the first bath should be returned to and fixed on the fibre. The "boiled-off liquor" serves as a restrainer in the subsequent dyeing vats. Such silks, particularly tussur silk, as contain lime in the sericin, require preliminary treatment with dilute hydrochloric acid before being boiled off, in order to remove this lime and prevent the formation of a lime soap.

The ungummed silk is then submitted to a "discharging" process—consisting in putting the hanks into a hemp bag and boiling for two or three hours with soap solution—and is finally washed. Occidental silks lose from 20 to 25 per cent. and Oriental silks from 18 to 22 per cent. in weight during these processes.

The bleaching proper of silks is now almost entirely effected by means of hydrogen peroxide, but treatment with sulphur dioxide either in stoves or in solution, after the manner described for wool, was, until lately, the method employed.

COTTON BLEACHING.—Cotton is bleached in the form of hanks of yarn if it is to be dyed in bright colours, or to be manufactured into sewing thread. Otherwise, and most frequently, it is bleached in the woven piece. In the latter case the loose fibres must be singed off, the process being effected by rapidly passing the piece over a red-hot roller, or a row of Bunsen burners, any persistent spark being extinguished by passage between damp rollers. The amount of time and trouble devoted to bleaching cotton cloth depends on the purpose for which it is being prepared, the number of processes through which the material is put being summed up under such trade names as "market bleach," "dyeing bleach," "madder bleach," &c. The titles sufficiently indicate the uses for which the material is destined, and the kind of variation in procedure will be realised when it is considered that it is a shorter process merely to oxidise the colouring matter until it is of the degree of whiteness suitable for white cotton cloth as put on the market, than to effect that thorough removal of matter foreign to the fibre which is essential to the production of good colours in dyeing and printing.

In the scouring of cotton, the cloth is first saturated with water by being passed between rollers in a tank through which water circulates. It is then boiled with a thin milk of lime, for some hours, in a closed "kier," which is a cylindrical vessel of boiler plate, in which the goods are packed on a cast-iron grating, and into which steam is injected at a pressure of 10 to 70 lbs.

above that of the atmosphere. By an appropriate arrangement the liquor which has percolated through the goods is intermittently raised by the steam pressure to the top of the kier, and again sparged on to the cotton. This process is the "lime-boil" or "lime-bowk." The lime saponifies fatty, waxy and resinous matters adhering to the cloth; the lime soaps being insoluble, the next process consists in decomposing these by dilute hydrochloric acid, into a bath of which, after a wash with water, the goods are passed, the operation being known as the "lime-sour" or "grey-sour." The fatty acids, liberated by the hydrochloric acid, are next dissolved by boiling in a pressure kier with caustic soda or carbonate of soda (5 to 6 per cent. of the weight of the goods), and rosin soap (corresponding with 1·5 to 2 per cent. of rosin also reckoned on the weight of the goods). The goods are now washed and boiled with soda ash, this "ley-boil" being several times repeated when the best bleaching for dyeing is required. A thorough washing completes the scouring process, and it is of interest to note that the scoured cotton is frequently darker in colour than it was before it was treated.

With regard to the chemistry of cotton scouring, it might be supposed that since the lime soaps formed in the lime-boil are decomposed in the subsequent acid bath, thus leaving the fatty acids to be saponified with soda, it would suffice to treat the cloth directly with soda, a custom which is, indeed, practised in the Mather and Platt process. It appears, however, that the formation of a soap from the liberated fatty acids, *in situ*, facilitates the saponification of any remaining fat by treatment with caustic soda; besides, lime is a more suitable, because cheaper, base than soda for the preliminary saponification.

The bleaching or "chemicking" of the cotton consists in passing the scoured goods through a very dilute solution (specific gravity about 1·0025 or ¼° Twaddell) of chloride of lime (bleaching powder), and then wringing them out and exposing them in heaps to the action of the air for two or three hours, care being taken that they do not dry. A bath of dilute sulphuric acid (1° to 1½° Twaddell = specific gravity 1·005 to 1·0075), known as the "white-sour," and a thorough washing complete the process, unless a repetition be deemed desirable. While the cotton wet with the solution of chloride of lime is exposed to the air, hypochlorous acid (HClO) is liberated by the atmospheric carbonic acid; this oxidises the colouring matter of the cotton to colourless products, the oxidation being completed by the chlorine which is evolved when the still undecomposed bleaching liquor comes in contact with the dilute acid of the white-sour—

$$\underbrace{Ca(OCl)_2 + CaCl_2}_{\text{Solution of bleaching powder.}} + 2H_2SO_4 = 2CaSO_4 + 2H_2O + Cl_4.$$

The dilute acid also dissolves the calcium carbonate which is deposited in the fibre during the air exposure.

Lunge proposes to effect the liberation of hypochlorous acid and simultaneous formation of calcium acetate by applying acetic acid before or after the bleaching liquor. When the hypochlorous acid gives up its oxygen to the colouring matter of the cloth, hydrochloric acid is formed; this would react with the calcium acetate, setting free acetic acid which would then perform the same cycle of reactions.

(1) $\underset{\text{Acetic acid.}}{2CH_3COOH} + Ca(OCl)_2 = \underset{\text{Calcium acetate.}}{(CH_3COO)_2Ca} + 2HOCl.$

(2) $2HOCl = 2HCl + O_2.$

(3) $(CH_3COO)_2Ca + 2HCl = CaCl_2 + 2CH_3COOH.$

If this treatment with acetic acid be substituted for the exposure to air, the advantage accrues that the soluble salt, calcium acetate, remains to be washed out in place of calcium carbonate which is insoluble in water.

It has been proposed to bleach by means of the liquor produced by the electrolysis of magnesium chloride (the Hermite process). When an electric current is passed through a solution of this salt, chlorine is evolved at the anode, and magnesia and hydrogen at the cathode. If means be taken for the suppression of the hydrogen, the chlorine acting on the magnesia yields a solution of magnesium hypochlorite, which may be applied similarly to the chloride of lime usually employed. The liquor, after it has done its work of bleaching, and its oxidising effect has been expended, is returned to the decomposing cells and again electrolysed. As magnesium hypochlorite is more unstable than calcium hypochlorite, free hypochlorous acid is more readily derived from the former, and thus the rate of bleaching is increased. The process, though said to be in successful operation in France, has proved a failure in this country.

For the production of a full white "market bleach" it is frequently necessary to correct the yellow tint of the bleached goods by the addition of a small quantity of ultramarine. It must be remembered that the oxidising action of chloride of lime is not without effect on the cellulose itself, so that the use of a strong solution of bleaching powder is not permissible.

LINEN BLEACHING.—As has been already indicated (p. 261), retted flax fibre contains much more matter of non-cellulosic character than is contained in cotton; it follows that the processes of scouring and bleaching linen are more operose than are those involved in the treatment of cotton. It is found useful in the case of linen to retain to a certain extent the old system of grass bleaching; otherwise the operations are in the main identical with those used for cotton, low-pressure kiers being generally employed. In common practice the yarn or cloth is subjected to the lime-boil, grey-sour and ley-boil described for cotton, and, after having been washed, is spread in a field for

from two to seven days; it is then chemicked in chloride of lime and soured. The ley-boil, exposure and chemicking are repeated as often as may be necessary in order to produce the desired tint, the "full bleach" requiring a longer time than the "half" or "quarter" bleach. Three to six weeks is an average time.

The chemistry of these processes when applied to linen is similar to that expounded under the head of cotton bleaching. The beneficial effect of exposure on grass may perhaps be attributed to a species of fermentation, enhanced by the action of light, and similar to that which is useful in the retting process (p. 261). Such a fermentation may decompose pectous substances, rendering them more easily attacked by the subsequent treatment.

The substitution of potassium permanganate for chloride of lime solution has been proposed in linen bleaching. The grass-exposed goods are to be steeped in a solution of this oxidant, and then passed through a solution of sulphurous acid, which reduces and dissolves deposited oxides of manganese; acidified peroxide of hydrogen may fulfil the function of the sulphurous acid, since this peroxide behaves as a reducing agent to the higher oxides of manganese.

JUTE BLEACHING.—The specific nature of the jute fibre (p. 262) renders its complete bleaching without undue tendering a difficult task. It is fortunate that jute fibre which has only been bleached to a cream colour can still be dyed of brilliant hues, so that the term "full bleach" as used for jute implies the production of this colour, the "half bleach" finishing at a straw coloured shade.

It is not usual to scour jute yarn with alkali before bleaching it, since the loss of weight due to the action of the alkali is not sufficiently compensated by the improvement in value of the finished product. A slight treatment with alkali and soap may be necessary, however, when much oil has been used in manufacturing the yarn. The principle involved in the common method of bleaching is to submit the fibre to the action of a comparatively strong liquor at first, and, when the most easily attacked impurities have been thus acted upon, to transfer it to weaker liquors, where there is little risk of the fibre being tendered. The first bath contains bleach amounting to 18 per cent. of the weight of the jute, the second bath contains 10 per cent. of bleach, and the third 5 per cent., calculated on the same basis. The yarn remains for half an hour in each bath, and the temperature is maintained at 120° F. = 49° C. For a full bleach, slightly stronger liquors are employed. After immersion in these baths, the yarn is soured in dilute sulphuric acid (1° Twaddell) for half an hour, and is then washed and dried. The jute suffers a loss of weight amounting to some 6 to 8 per cent.

For bleaching jute in the piece, Cross and Bevan recommend a silicate of soda bath for preliminary treatment, and the use of a bleach liquor made by adding soda ash to a solution of bleaching powder (0·7 per cent. of available chlorine), and containing, therefore, sodium hypochlorite; a sulphuric acid sour and the usual washing complete the process.

Hemp, when bleached at all, is treated like linen. China grass is bleached by the methods employed for cotton.

CHAPTER XIII.

COLOURING MATTERS, DYEING, AND PRINTING.

It is the object of the dyer to produce a uniform colour in the textile material to be dyed. Such colour must be "fast"—*i.e.*, insoluble—not mechanically detachable, and resistant to the bleaching action of light. In order that the colour may impregnate the fabric it is essential that it be applied in solution; thus a dyestuff may be broadly distinguished from a pigment by its solubility in an appropriate menstruum, generally water. When a dyestuff has been applied to the fibre and constitutes a fast colour, it has become a pigment. A convenient distinction may be drawn between a dyestuff and a dye. The former is not necessarily coloured, although even when not coloured it is capable of furnishing a pigment when fixed upon the fibre; this pigment is the dye. The substance necessary to convert a dyestuff into a dye fast on the fibre is termed a mordant; some fibres themselves act as mordants. If the above differentiation between dyestuffs and dyes be allowed, the fibre must be regarded as the mordant in all cases where it is dyed directly, even when, as in the case of direct cotton dyestuffs, the "affinity" between the fibre and the dyestuff is comparatively feeble.

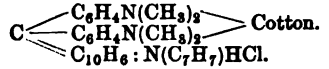
The difficulty of arriving at a general explanation of the rationale of dyeing arises from the facts (1) that fibres differ very greatly both chemically and mechanically, and (2) that dyes are also widely diverse in character, ranging from insoluble pigments, produced irrespective of the chemical nature of the fibre, to definite chemical compounds with the fibre (or some constituent of the fibre) itself.

In speaking of dyestuffs it is found convenient to classify them as "substantive" and "adjective," the former term being applied to dyestuffs which need no addition to fix them upon the fibre, and the latter to such as require a "mordant" to cause their conversion into dyes. In the same way the dyes produced may be spoken of as "substantive dyes" and "adjective dyes."

The need for a mordant depends upon the chemical nature of the fibre as well as upon that of the dye. The capability of fibres to fix, by actual combination, dyestuffs having a distinct

acid or basic character, is dependent upon the presence in the fibre of certain basic or acid activities. The most notable instance is found in the case of wool, the investigation of which has revealed the existence of an amido-acid (*i.e.*, a substance capable of functioning both as an acid and as a base), either as a constituent of the fibre or as a product of its decomposition in the dye-bath. The wool, according to this view, may be represented as $W\begin{cases}NH_2\\ \\COOH\end{cases}$; where W represents the constituents of the wool other than those giving it its acid and basic character. Such a compound has been obtained from wool by heating with an alkali, and has had the name **lanuginic acid** ascribed to it. It is soluble in hot water and precipitates both acid and basic dyestuffs, forming lakes (see *Pigments*, Vol. II., Chap. XV.). Silk fibre displays functions similar to those of wool, its acid character being strongly marked. Cotton, on the other hand, is a far less active substance than the animal fibres, and displays but a trifling affinity for dyestuffs, whether acid or basic. Since the constitution of wool has to a certain extent been elucidated, the chemical theory of dyeing, according to which substantive dyestuffs become dyes on the fibre by union therewith, has been generally accepted so far as wool is concerned. In the case of silk there is not only less direct evidence of union of the fibre and dyestuff, but there is also some indication of another cause of dyeing (asserted by some to provide a general explanation of the rationale of dyeing—the so-called "physical" theory of dyeing), viz., the action of the fibre as a solvent for the dyestuff, which it holds in the form of a solid solution. For example, when silk dyed with magenta is immersed in alcohol, the magenta is extracted, but, on diluting the alcohol with water and thus diminishing its solvent power for the magenta, the colouring matter returns to the silk; the deduction made is that silk is a worse solvent for magenta than is alcohol, but a better solvent than diluted alcohol, and that the retention of the magenta by one or the other solvent (silk or alcohol) depends on their relative solvent power, and is not due to chemical combination with the silk in any more definite sense than with the alcohol. Cotton, however, does not readily lend itself to either of these explanations singly. The structure of cotton fibre has been already described (see *Textiles*, Vol. II., p. 260). Chemically, it does not appear to possess in any degree either basic or acid properties, partaking rather of the nature of an aldehyde; but it is well known that cotton forms unstable compounds with basic oxides—*e.g.*, lead oxide—and a similar slight acid tendency is observed in the behaviour of cotton towards basic substantive dyestuffs, such as the substance known as "night blue." In this case, however, the cotton does not

displace the acid of the salt constituting the dyestuff, but combines with the salt as a whole, this combination being rendered possible by the fact that the salt contains methylamido groups other than that satisfied by the acid radicle of the salt. Thus, cotton dyed with night blue may be written diagrammatically



The absence of definite acid properties of cotton, however, lends some support to the view that its absorption of certain substantive dyes is due to its acting as a solid solvent in the manner already described in the case of silk. A similar explanation might be offered to account for the mordanting action of tannin on cotton. Immersion of the cotton in a solution of tannin frequently precedes the dyeing process. The tannin itself is but loosely attached to the cotton, for the tannin-treated cotton loses tannin when immersed in water or even weak solutions of tannin. Obviously, however, this fact is not inconsistent with the view that cotton has a feebly basic character, which allows it to form a loose combination with the tannin. The fixation of a basic dyestuff by the tannin is seen to need no explanation when the acid character of this substance is remembered. The activity of cotton as an acid material can be greatly enhanced by any process of an oxidising character, as in "chemicking" (see *Bleaching*, Vol. II., p. 266), the oxycellulose* formed readily fixing basic dyestuffs. In spite of the feeble activity (whether acid or basic) of cotton fibre towards dyestuffs, certain synthetic substances—the benzidine derivatives—form fairly fast substantive dyes on cotton. In this case it has been suggested that the dyes enter the fibre—presumably from their high osmotic pressure—in hot solution, and are there deposited on the cell walls as the fibre cools on withdrawal from the bath. The theory of solid solution is hardly applicable in this instance, because gelatinised nitrated cellulose cannot be thus dyed, although nitrated cellulose, not gelatinised and still possessing the structure of cotton fibre, can be dyed in this manner.

It will be obvious that in cases of adjective dyeing, defined in its broadest sense as dyeing induced by the co-operation of at least two agents, no special explanation of the cause of dyeing any fibre is requisite. Thus fibre of any kind may be dyed by successive immersion in a solution of a lead salt and in one of a chromate, lead chromate being precipitated in the fibre and retained on account of its insolubility.

* The formula $C_{18}H_{26}O_{16}$ has been assigned to this substance.

A. COLOURING MATTERS.—Dyestuffs may be classified into a few broad groups.

(1) Organic synthetic dyestuffs. An exhaustive classification is necessarily very lengthy, but the chief classes may be given as follows:—(*a*) Nitro-compounds. (*b*) Azo-compounds. (*c*) Quinone derivatives. (*d*) Triphenylmethane derivatives. (*e*) Azine compounds.

(2) Organic natural dyestuffs.

(3) Mineral dyestuffs.

(1) **Organic Synthetic Dyestuffs.***—In speaking of these it is necessary to refer to the theory of Witt, who considers that certain groups (**chromophores**), such as NO_2 and $N{=}N$, confer upon hydrocarbon residues of the ring type properties which enable them to become dyestuffs when certain acid or basic groups are introduced. The compound consisting of a ring hydrocarbon residue and a chromophore is called a **chromogen**, and the acid or basic group which transforms it into a dyestuff is termed an **auxochrome**. This theory has proved useful as a guide in the synthesis of new dyestuffs.

(*a*) **Nitro-compounds.**—The nitro-group is the chromophore in the case of these bodies, and the auxochrome is generally either OH or NH_2, the dyestuffs of this class being for the most part nitrophenols and nitro-derivatives of amines. They are formed by the process of nitration, the raw materials being aromatic phenols and amines. The chief dyestuffs of this class are **picric acid** (trinitrophenol), dinitro-*α*-naphthol (**Martius yellow**), and the sodium salt of its sulphonic acid (**naphthol yellow**), and hexanitrodiphenylamine (its ammonium salt being called **aurantia**). The foregoing are decidedly acid in character. The preparation of picric acid, which may be taken as a type of nitration, was at one time carried on by direct treatment of phenol with strong nitric acid, but is now performed by sulphonating phenol, by heating with sulphuric acid, and treating the resulting phenol-sulphonic acid with nitric acid of moderate strength (specific gravity 1·3). Picric acid is a common product of the nitration of organic substances. It is a bright yellow bitter substance, sparingly soluble in cold water and readily soluble in alcohol and ether. It melts at 122·5° C. = 252° F. Its use as a dyestuff is now limited, but it finds application in the manufacture of explosives (see Vol. II., Chapter XVII.).

(*b*) **Azo-compounds.**—These dyestuffs contain the chromophore —N : N— uniting two ring nuclei. The auxochromes OH and NH_2 serve to convert the azo-compounds into dyestuffs.

$C_6H_5 \cdot N : N \cdot C_6H_5$. Azobenzene.

$C_6H_5 \cdot N : N \cdot C_6H_4(NH_2)$. Amidoazobenzene (a dyestuff).

The dyestuffs of this class are produced by the reaction between

* In the following pages the nomenclature and classification adopted are, in the main, those of Nietzki (*Organische Farbstoffe*, Berlin, 1894).

a diazo-compound (*e.g.*, diazobenzene chloride, $C_6H_5 \cdot N : N \cdot Cl$), and a phenol or an amine, the general process of manufacture consisting in first preparing the diazo-compound, by treating the well-cooled solution of an amine with sodium nitrite and hydrochloric acid, and allowing the solution to flow into one of the phenol or its sulphonic acid in presence of excess of alkali. The dyestuff is finally thrown out of solution by the addition of common salt. Somewhat different processes are necessary for combining the diazo-compound with an amine—*e.g.*, the use of alcohol as a solvent may be essential. The reactions taking place in both cases are typified by the following examples of dyestuffs prepared from aniline. It will be remembered that the action of nitrous acid on the salts of aromatic amido-compounds (amines) at a low temperature leads to the formation of the salt of the corresponding diazo-compound :—

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5 \cdot NH_2, HCl} + \underset{\text{Nitrous acid.}}{NO \cdot OH} = \underset{\text{Diazobenzene chloride.}}{C_6H_5 \cdot N : N \cdot Cl} + 2H_2O.$$

Since nitrous acid is a very unstable substance, it is better in practice to mix the amido-compound (amine) with sodium nitrite, and to add hydrochloric acid to liberate nitrous acid *in situ* ; the process is known as diazotising. No attempt is made to isolate the diazobenzene chloride from the solution.

If an hydroxyazo-dyestuff is to be prepared, the solution of the diazobenzene chloride is run into a well-cooled solution of the calculated quantity of the phenol (*e.g.*, $C_6H_5 \cdot OH$) dissolved in an alkali ; the following equation is typical of the change :—

$$C_6H_5 \cdot N : N \cdot Cl + \underset{\text{Sodium phenol.}}{C_6H_5 \cdot ONa} = \underset{\text{Benzeneazophenol.}}{C_6H_5 \cdot N : N \cdot C_6H_4(OH)} + NaCl.$$

If an amidoazo-dyestuff is to be produced, a cooled solution containing the calculated quantity of the amido-compound (*e.g.*, metaphenylene-diamine) is run into the solution of diazobenzene chloride :—

$$C_6H_5 \cdot N : N \cdot Cl + \underset{\text{Metaphenylene-diamine.}}{C_6H_4(NH_2)_2} = \underset{\text{Diamidoazobenzene hydrochloride.}}{C_6H_5 \cdot N : N \cdot C_6H_2(NH_2)_2, HCl.}$$

The diamidoazobenzene hydrochloride is soluble in water, and must be salted out ; it constitutes the dyestuff known as chrysoidine, which produces an orange yellow on wool.

The hydroxyazo-dyestuffs are generally insoluble, and must be converted into sulphonic acids by treatment with strong sulphuric acid, or obtained as sulphonic acids by the use of the sulphonic acid of one or other of their constituents—*e.g.*, phenol-sulphonic acid, $C_6H_4(OH)(SO_2OH)$.

Of such azo-dyestuffs as are of importance may be mentioned the amidoazo-dyestuff, methyl orange (helianthin), much used as

an indicator in alkalimetry. It is the sodium salt of dimethylamidoazobenzene sulphonic acid,

$$C_6H_4(SO_3Na)\cdot N:N\cdot C_6H_4\cdot N(CH_3)_2.$$

An example of an hydroxyazo-dyestuff is **tropæolin Y** (an orange dyestuff), the sodium salt of phenolazobenzene sulphonic acid, $C_6H_4(OH)\cdot N:N\cdot C_6H_4(SO_3Na)$. **Tropæolin O** is a dyestuff which dyes silk a golden yellow, and is obtained from resorcinol and diazobenzene chloride; it thus contains two OH groups, $C_6H_4(SO_3Na)\cdot N:N\cdot C_6H_3(OH)_2$. The hydroxy-derivatives of naphthalene (naphthols) may be used; **crocein orange**, for example, is the sodium salt of benzeneazo-β-naphthol sulphonic acid, $C_6H_5\cdot N:N\cdot C_{10}H_5(OH)(SO_3Na)$, and is prepared from diazobenzene chloride and β-naphthol sulphonic acid. Such dyes are faster when derived from β-naphthol than when derived from α-naphthol.

The foregoing azo-dyestuffs can be used in an acid bath for wool and silk, but are not fitted for cotton, as they fail to form lakes with appropriate mordants. The two basic azo-dyestuffs which are commonly used, namely, chrysoidine (*v.s.*), and **Bismarck brown** [triamidoazobenzene hydrochloride,*

$$C_6H_4(NH_2)\cdot N:N\cdot C_6H_3(NH_2)_2,HCl],$$

are capable of fixation on cotton mordanted with tannic acid.

Tetrazo-dyestuffs are such as contain the $\cdot N:N\cdot$ group twice.†

* Much of the commercial Bismarck brown consists of the compound $C_6H_4[\cdot N:N\cdot C_6H_3(NH_2)_2]_2$, a disazo-derivative (*v.i.*).

† The whole nomenclature of azo-dyestuffs is of an arbitrary character. Thus the compound $C_6H_5\cdot N:N\cdot C_6H_5$ was originally termed azobenzene, whereas the substance $C_6H_5\cdot N:N\cdot Cl$ was called diazobenzene chloride, although the number of nitrogen (azote) atoms is identical in the two compounds. The expression tetrazo-compounds is commonly applied to substances containing four N atoms, whereas the term disazo-compounds is used for compounds containing the same number of N atoms, the prefix applying in this case not to the number of atoms but to the number of $\cdot N:N\cdot$ groups. Under these circumstances the following empirical arrangement may be adopted, R standing for a ring nucleus:—

(1) Monazo-compounds of the form $R\cdot N:N\cdot R$;
(2) Disazo-compounds of the type $R\cdot N:N\cdot R\cdot N:N\cdot R$;
(3) Diazo-compounds of the form $R\cdot N:N\cdot Cl$;
(4) Trisazo-compounds $R\cdot N:N\cdot R\cdot N:N\cdot R\cdot N:N\cdot R$;
(5) Tetrazo-compounds $R\cdot N:N\cdot R\cdot R\cdot N:N\cdot R$.

It will be noticed that in the monazo-compounds the $\cdot N:N\cdot$ group is attached to two ring nuclei; in the disazo-compounds two $\cdot N:N\cdot$ groups are attached to three ring nuclei; in the diazo-compounds a single $\cdot N:N\cdot$ group is attached to one ring nucleus, the other bond of the group being satisfied with an acid radicle, *e.g.*, Cl; in the trisazo-compounds there are three $\cdot N:N\cdot$ groups attached to four ring nuclei; whilst in the tetrazo-compounds two $\cdot N:N\cdot$ groups are attached to four ring nuclei, two of which are themselves united.

They are of three types:—(1) Those containing the two ·N:N· groups and the auxochrome (*e.g.*, NH_2 or OH) attached to the same benzene nucleus—*e.g.*, phenoldisazobenzene,

$$C_6H_5\cdot N:N\cdot C_6H_3(OH)\cdot N:N\cdot C_6H_5$$

they are often called disazo-compounds. (2) Those having the two ·N:N· groups attached to the same benzene ring, while the auxochrome is in another ring—*e.g.*, benzeneazobenzeneazophenol,

$$C_6H_5\cdot N:N\cdot C_6H_4\cdot N:N\cdot C_6H_4\,(OH).$$

(3) Those of the benzidine class, in which the two ·N:N· groups are in different rings, which are united.

The dyestuffs of the first of these groups are obtained by the action of a diazo-salt on an amido- or hydroxy-azobenzene derivative; thus from diazobenzene chloride and dihydroxyazobenzene (resorcinolazobenzene), **resorcinoldisazobenzene** is prepared:—

$$C_6H_5\cdot N:N\cdot Cl + C_6H_5\cdot N:N\cdot C_6H_3\,(OH)_2$$
$$= \underset{\text{Resorcinoldisazobenzene.}}{C_6H_5\cdot N:N\cdot C_6H_2\,(OH)_2\cdot N:N\cdot C_6H_5} + HCl$$

In practice NaOH would be present to take up the HCl. The members of the second group are obtained by diazotising (p. 274) amidoazobenzene derivatives (or homologues thereof), and combining the products with amines or phenols:—

$$(1)\ \underset{\text{Amidoazobenzene hydrochloride.}}{C_6H_5\cdot N:N\cdot C_6H_4(NH_2),HCl} + NO\cdot OH$$
$$= C_6H_5\cdot N:N\cdot C_6H_4\cdot N:N\cdot Cl + 2HOH$$

$$(2)\ \underset{\text{Azobenzenediazochloride.}}{C_6H_5\cdot N:N\cdot C_6H_4\cdot N:N\cdot Cl} + C_6H_5\cdot ONa$$
$$= \underset{\text{Benzeneazobenzeneazophenol.}}{C_6H_5\cdot N:N\cdot C_6H_4\cdot N:N\cdot C_6H_4(OH)} + NaCl.$$

Biebrich Scarlet, made by diazotising amidoazobenzene disulphonic acid and combining the product with β-naphthol, is an example of a commercial dyestuff of this class; it contains sodium benzeneazobenzeneazo-β-naphthol disulphonate,

$$C_6H_4(SO_3Na)\cdot N:N\cdot C_6H_3(SO_3Na)\cdot N:N\cdot C_{10}H_6(OH).$$

The isomeric compound,

$$C_6H_4(SO_3Na)\cdot N:N\cdot C_6H_4\cdot N:N\cdot C_{10}H_5(OH)(SO_3Na),$$

is **crocein scarlet.**

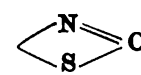
The dyestuffs of these two classes of the so-called tetrazo-dyestuffs dye wool and silk in acid baths, but can only be used for cotton with aluminium mordants, in which case they yield feeble and fugitive shades.

Members of the third class are obtained by diazotising benzidine $\begin{matrix}C_6H_4\cdot NH_2\\ |\\ C_6H_4\cdot NH_2\end{matrix}$ and its derivatives or their homologues, and combining the product, of the form $\begin{matrix}C_6H_4\cdot N:N\cdot Cl\\ |\\ C_6H_4\cdot N:N\cdot Cl\end{matrix}$ (tetrazo-diphenyl chloride), with amines and phenols.

Congo red (used as an indicator and a dyestuff) is the type of this class, and is prepared by combining diazotised benzidine with α-naphthylamine sulphonic acid, the product having the formula

$$\begin{matrix}C_6H_4\cdot N:N\cdot C_{10}H_5(SO_3Na)(NH_2)\\ |\\ C_6H_4\cdot N:N\cdot C_{10}H_5(SO_3Na)(NH_2).\end{matrix}$$

These benzidine tetrazo-dyestuffs are notable as being "direct cotton colours"—that is, they will dye cotton in fairly fast shades without the aid of mordants. It is only in accord with the general remarks at the beginning of this chapter that the cotton absorbs the dyestuff more readily from a strong dye-bath than from a weak one, and that the presence of any substance in the bath which will diminish the solubility of the dyestuff, such as salt, will facilitate the dyeing.

A dye closely connected with those of the azo-group is primuline, which is the sodium sulphonate of "primuline base," the product of the action of sulphur on paratoluidine at a high temperature. The chromophore of the primuline-derived colours appears to be the group  .

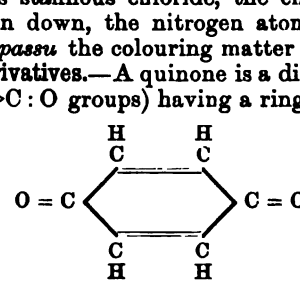
The primuline base itself contains three such groups, being produced by the condensation of four molecules of paratoluidine with three atoms of sulphur. Cotton can be directly dyed with primuline (yellow), which has a considerable affinity for its fibre, but primuline has a wider application for producing "ingrain" colours. The processes for producing ingrain colours—consisting in forming the dye in the fibre, in similar manner to that adopted for the precipitation of insoluble dyes, *e.g.* $PbCrO_4$, in the fibre—are specially advantageous in the case of azo-dyes, which may be prepared in the fibre by one of two methods—(1) the fabric is passed successively through baths containing a phenol in alkaline solution and a solution of a diazo-compound respectively; (2) the fabric is impregnated with solutions of a diazo-compound and a phenol, which are then made to react by passage through an alkali. The great advantage of this method for azo-colours resides in the fact that when these are used for dyeing in the customary way they must be used as sulphonic acids on account

of their insolubility, and this necessity is avoided by the processes described above; wool and silk have an affinity for such sulphonic acids, but cotton is unable to fix them *per se*.

Inasmuch as primuline contains an NH_2 group, it is capable of diazotisation and of subsequent combination with a phenol or an amine. It thus lends itself to the production of ingrain colours, which is best effected in this case by first dyeing the fibre with primuline, then diazotising this *in situ* by passage through a bath of sodium nitrite and an acid, and finally treating the diazotised fibre in a bath of a phenol or an amine. The diazotised primuline is decomposed by light, and cannot be subsequently developed in a phenol bath. It can, therefore, be used for photographic printing, both on fabrics and films.

Azo-dyes are characterised by the ease with which they are reduced to the corresponding amido-compounds by the action of such a reagent as stannous chloride, the chromophore $N = N$ being thus broken down, the nitrogen atoms becoming singly linked, and *pari passu* the colouring matter decolorised.

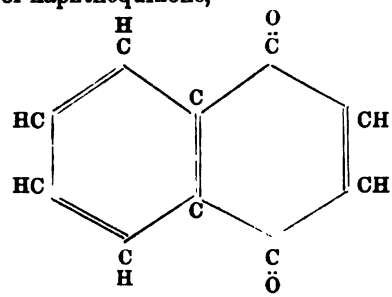
(*c*) **Quinone Derivatives.**—A quinone is a diketone (a derivative containing two $>C:O$ groups) having a ring nucleus—*e.g.*,



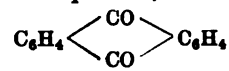
Armstrong has suggested that the colour of coloured substances is dependent upon their possession of a structure analogous to that of quinone ("quinonoid structure"). The oxygen of the $>C:O$ groups may be replaced by other elements or groups, provided that the double linking be preserved and the "quinonoid structure" of the product maintained. Another characteristic of the quinonoid structure is the existence in the compound of an unsaturated ring nucleus, such as that of benzene, containing six elements, two of which are the ketone or modified ketone groups. Great difficulty has been experienced in bringing all coloured substances within the limits demanded by a quinonoid structure, and the hypothesis is accordingly still not fully substantiated. A substance such as azobenzene, $C_6H_5 \cdot N : N \cdot C_6H_5$, needs profound alteration of its accepted formula to cause it to conform with the requirements of the theory.

Quinones generally are powerful chromogens; the $>C:O$ groups or their equivalents are the chromophores, and the chief auxochrome is hydroxyl, so that hydroxyquinones are the commonest dyestuffs of this class. In quinones derived from the benzene series the hydroxyquinones and the tetrahydroxyquinones act as feeble adjective dyes, but the dihydroxyquinones are incapable

of dyeing to more than a slight extent. In two-ring derivatives, such as those of naphthoquinone,



and in derivatives of anthraquinone,



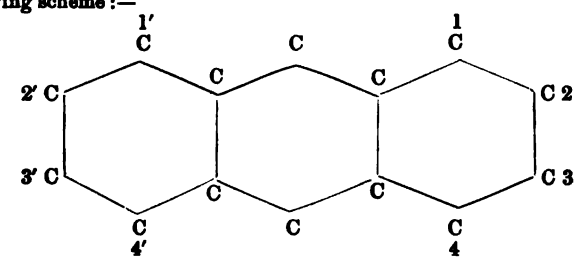
those hydroxy-derivatives which have an hydroxyl group in a position adjacent to that of the quinonic oxygen are alone capable of acting as dyestuffs, and usually there must be two hydroxyl groups present, adjacent to each other, one of which is adjacent to the quinonic oxygen. The chief members of the group of quinone dyestuffs are given below; they are mainly used as adjective dyestuffs, for although capable of behaving as substantive dyestuffs, the dyes produced are comparatively feeble.

Dihydroxynaphthoquinone, $C_{10}H_4(OH)_2O_2$ (naphthazarine; alizarin black), is prepared by heating α-dinitronaphthalene with strong sulphuric acid and zinc. The dyestuff is the sodium bisulphite compound.* Quinone dyestuffs from benzene or naphthalene are of little importance, but those from the next higher series (anthracene series) are largely used.

Hydroxyanthraquinones.—In accordance with the statement already made relative to the influence of the hydroxy-groups in quinonic derivatives of the naphthalene and anthracene series, it follows that only such polyhydroxyanthraquinones as have hydroxyl groups in the 1 : 2-positions† are dyestuffs. The

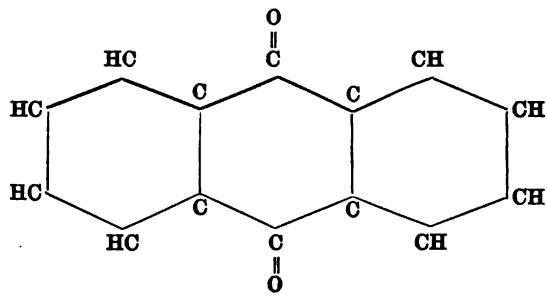
* It is characteristic of the ketones, as of the aldehydes, to form additive compounds with bisulphites.

† The orientation of anthracene and its derivatives is expressed by the following scheme:—



dihydroxyanthraquinone in which the hydroxyl groups have these positions is alizarin.

Alizarin was formerly obtained from madder. Madder is the root of *Rubia tinctorum*, formerly much cultivated in Italy and France. The roots are allowed to remain in the ground after the leaves have been removed, during which sojourn (frequently lasting for years) a fermentation occurs, whereby alizarin is developed by the hydrolysis of the glucoside ruberythrin, $C_{26}H_{28}O_{14}$, thus, $C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_6O_2(OH)_2 + 2C_6H_{12}O_6$. The ferment inducing this change is called erythrozyme. Other glucosides are present which also yield alizarin, in addition to purpurin and isopurpurin. The amount of dried madder obtained is about 25 per cent. of the weight of the original root. The total colouring matter is about 3 per cent. of the weight of the madder. The madder is prepared for the market in various forms; thus "garancin" is prepared by soaking the madder in water, adding dilute sulphuric acid to the moist mass, and boiling with steam whereby the glucosides are hydrolysed; "flowers of madder" is prepared by treating the madder with water or dilute sulphuric acid to remove yellow colouring matters. Madder is still used to a small extent for dyeing wool, but it has been almost driven out of the field (especially for cotton) by artificial alizarin. Alizarin is now made from anthracene $C_{14}H_{10}$, which is purified by distillation in a current of steam, and the finely divided product treated with the calculated quantities of sodium bichromate and sulphuric acid, whereby it is oxidised to anthraquinone



By the use of a regulated quantity of the reagents, oxidation of contaminating hydrocarbons is avoided, and a fairly pure product obtained. The chrome-alum left by the reaction of the sulphuric acid on the bichromate of soda is precipitated by excess of lime and the mixture of chromium oxide, lime, and calcium sulphate roasted, calcium chromate being formed, which is converted into sodium chromate by treatment with sodium carbonate solution.

The anthraquinone is purified by dissolution in two or three times its weight of sulphuric acid at 110° C. = 230° F., and crystallisation by cooling, the residue being precipitated by the addition of water. The impurities in the anthraquinone are converted into sulphonic acids by this treatment, and remain in solution. Sublimation in a current of steam completes the purification process. The anthraquinone is next treated with fuming sulphuric acid, whereby a mixture of mono- and disulphonic acids of anthraquinone, $C_{14}H_7O_2(HSO_3)$ and $C_{14}H_6O_2(HSO_3)_2$, results. The temperature of sulphonation is kept low in order to obtain a large yield of monosulphonic acid, which alone yields alizarin, although the disulphonic acid is not useless, since from it are ultimately formed isopurpurin and flavopurpurin. The next step consists in saturating the sulphonic acids with calcium carbonate, and converting the calcium sulphonates into sodium salts by treatment with sodium carbonate. The intermediate use of calcium carbonate effects a saving of sodium carbonate by neutralising the excess of sulphuric acid with a cheaper material. The sodium sulphonates are mixed with three times their weight of caustic soda (dissolved in water) and some sodium chlorate, in an iron pressure vessel provided with an agitator. The mixture is kept at a temperature of 180° to 210° C. = 356° to 410° F. for some days. During this time the sodium anthraquinone monosulphonate is converted into sodoxyanthraquinone, thus—

$$C_{14}H_7O_2(SO_2ONa) + 2NaOH = C_{14}H_7O_2(ONa) + Na_2SO_3 + H_2O.$$

This body is then oxidised by the sodium chlorate in presence of caustic soda into di-sodoxyanthraquinone (sodium alizarate).

$$C_{14}H_7O_2(ONa) + NaOH + O = C_{14}H_6O_2(ONa)_2 + H_2O.$$

The sodium anthraquinone disulphonates, which are mixed with the mono-compound, yield respectively the isomerides isopurpurin and flavopurpurin, each having the formula $C_{14}H_5O_2(OH)_3$. The melt is boiled with water, and the dyestuffs precipitated from the solution by the addition of hydrochloric acid, filter pressed, and made into a paste (containing about 20 per cent. of solid dyestuff) with water. Alizarin when once dried and anhydrous will not redissolve readily in water, whence the practice of selling it as a paste has arisen.

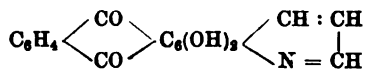
Nearly pure alizarin is used for dyeing blue shades of red, whilst an alizarin paste rich in isopurpurin and flavopurpurin is used for yellow shades. Alizarin is most widely used for dyeing and printing cotton. The fabric is mordanted in accordance with the colour required. The metallic mordants form salts (alizarates) containing the metals replacing the hydroxyl hydrogen. The colours range from red with alumina, to violet black with iron. The mordanted fabric is immersed in a vat containing

alizarin paste suspended in water, and the whole slowly boiled. Large quantities of alizarin are used for Turkey-red dyeing. In the original form of this process the fabric is saturated with an emulsion of rancid olive oil (*huile tournante*) in sodium carbonate solution, and exposed to the air, preferably at a somewhat elevated temperature. Oxidation of the oil ensues, and hydroxy-fatty acids are formed, which remain on the fibre after the superfluous oil has been washed off. The fabric is then treated with tannin in a sumach bath, and with aluminium acetate, when it is ready for dyeing with alizarin. The presence of lime in the alizarin bath is necessary, and, should the water be soft, lime must be supplied in the form of calcium acetate. The preliminary treatment with olive oil emulsion is tedious, and is now generally replaced by the use of Turkey-red oil (*q.v.*), the necessity for the oxidation of the fatty acids by prolonged exposure to air being thus removed. The rest of the process is similar to that described for the older method. The function of the oxidised oil, however obtained, is stated to be partly the formation of an aluminium fatty salt, which gives a finer red than alumina itself, and partly the protection of the colouring matter by a varnish-like film of oxidised fatty acids—an explanation lacking confirmation.

Tetrahydroxyanthraquinones, $C_{14}H_4O_2(OH)_4$.—The most important of these is "alizarin Bordeaux" (used for cherry red shades on aluminium mordants) obtained by the action of fuming sulphuric acid on dry alizarin and treatment of the product with hot water.

Alizarin cyanine is a pentahydroxyanthraquinone, and gives shades very similar to those of alizarin Bordeaux with alumina, but blue shades on chromium mordants.

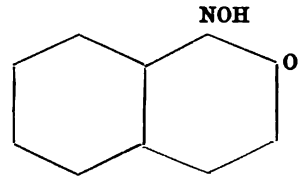
Alizarin blue S, or soluble alizarin blue, is an alizarin product of some importance as an indigo substitute. It is prepared by nitrating alizarin suspended and partially dissolved in glacial acetic acid. The product, β-nitroalizarin, $C_{14}H_5(NO_2)O_2(OH)_2$, is heated to 150° C. = 302° F., with sulphuric acid and glycerin, whereby it is converted into alizarin blue which is dihydroxyanthraquinone quinoline,



The sodium bisulphite additive compound of this, constitutes soluble alizarin blue. The presence of quinolinic nitrogen in alizarin blue gives it a feeble basic character. With chromium oxide as a mordant, the blue colour produced by soluble alizarin blue is comparable with that of indigo.

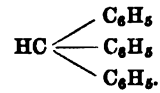
Another class of quinone derivatives consists of the **quinone-oximes**. These contain an $>NOH$ group in place of the O of one

of the C O groups characteristic of a quinone. Thus the naphthoquinoneoxime,

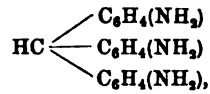


gives a green dye with iron mordants and a red with cobalt.

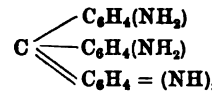
(*d*) **Triphenylmethane Derivatives.** — The triphenylmethane colouring matters are oxidation products of certain amido- and hydroxyl-derivatives of the substituted paraffin triphenylmethane,



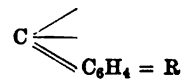
Thus, paraleucaniline,



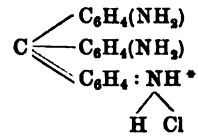
gives rise to pararosaniline,



when two hydrogen atoms are removed by oxidation. The chromophore in this chromogen is the quinonoid group



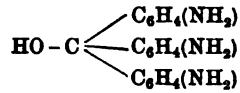
in which R is either : NH or O. The formula given above for pararosaniline does not represent an isolated compound, for it only exists in the salts of pararosaniline, of the form



the acid radicles of which constitute the auxochrome. When

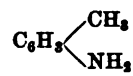
* There is some evidence in favour of regarding the salts of pararosaniline and its derivatives as having the form $Cl \cdot C:(C_6H_4NH_2)_3$, in which case they would partake of the nature of ethereal salts derived from the carbinol. This view requires confirmation.

the salts are treated with bases, a pararosaniline base, such as triamidotriphenyl carbinol,



is obtained.

This is a colourless substance, and on treatment with an acid yields a coloured salt, the acid radicle serving as an auxochrome as mentioned above. Differences of colour in the dyestuffs thus produced are caused by the introduction of hydrocarbon radicles as substitutes for the hydrogen of the amido-groups. Rosaniline, the basis of the commonest aniline dyestuff, magenta, differs from pararosaniline in that it contains an amidotolyl group,



in place of one of the amidophenyl groups, $C_6H_4(NH_2)$.

Although constitutionally the prefixed "para" refers to the position of the amido-groups in the benzene nuclei with respect to the methane carbon atom, yet the expression pararosaniline is arbitrarily used to distinguish this substance from the methyl substituted body of similar constitution.

The starting point for dyestuffs of this class ("aniline dyes") is benzene or a homologue. Modern practice requires the preparation of approximately pure hydrocarbons, chiefly C_6H_6, $C_6H_5(CH_3)$, $C_6H_4(CH_3)_2$, whereas formerly, mixtures of these were commonly used, such as "30 per cent. benzol" and "90 per cent. benzol" (Vol. II., p. 79). The hydrocarbon must first be converted into a nitro-derivative, which is then reduced to the corresponding amido-compound. The description of these processes as applied to benzene is as follows:—The benzene (about 1,000 lbs.) is charged into a vertical cast-iron cylinder and a mixture of 1,280 lbs. of nitric acid (specific gravity 1·39) and 1,790 lbs. of sulphuric acid (95 to 96 per cent.) is run in, in a very slow stream, the charge being agitated and the cylinder cooled until the whole of the acid has been added, when the temperature is allowed to rise to about 80° C. = 176° F. When the mixture has settled, the acid is drawn off and the nitrobenzene, $C_6H_5(NO_2)$, washed with water.

Nitrobenzene is a yellow oily liquid, boiling at 206° C. = 403° F., and having a specific gravity of 1·18. It has a characteristic, somewhat fragrant odour, and on this account is used for scenting common soaps, as a substitute for oil of bitter almonds. When it is to be thus employed it is redistilled and termed "essence of mirbane." When **dinitrobenzene** is required, the benzene is treated with two separate nitrating charges, and the temperature is allowed to rise more rapidly.

The isomeric dinitrobenzenes—bodies crystallising in yellow needles—are allowed to settle and are washed, first with cold water and finally with hot water.

Aniline is obtained by the reduction of nitrobenzene by iron in the presence of water and ferrous chloride, which acts as a carrying agent. When aniline was first made on a commercial scale, sufficient acid was used to supply, by the action upon it of the iron, enough hydrogen to convert $C_6H_5(NO_2)$ into $C_6H_5(NH_2)$. In modern practice only enough acid (hydrochloric acid) is used to start the reaction, which then proceeds thus:—The small quantity of hydrochloric acid reacts with the iron to form (potential) hydrogen (which reduces nitrobenzene to aniline) and ferrous chloride, which in its turn reduces a further quantity of nitrobenzene to aniline, hydrated ferric oxide and ferric chloride being formed. The ferric compounds are reduced to ferrous compounds by the metallic iron, and then the ferrous chloride goes through the cycle of reactions already described. The following equations may be taken as representative of the changes involved:—

$$Fe + 2HCl = FeCl_2 + H_2$$
$$C_6H_5(NO_2) + H_6 = C_6H_5(NH_2) + 2H_2O$$
$$C_6H_5(NO_2) + 6FeCl_2 + H_2O = C_6H_5(NH_2) + 2Fe_2Cl_6 + Fe_2O_3$$
$$Fe_2Cl_6 + Fe = 3FeCl_2$$
$$4Fe_2O_3 + Fe = 3Fe_3O_4.$$

The final products are therefore aniline, hydrated ferroso-ferric oxide and ferrous chloride.

The process of manufacture is conducted in a cast-iron still provided with an agitator and a hopper for the gradual introduction of the iron (borings). A portion of the iron is first introduced, steam is injected, and the hydrochloric acid run in. The nitrobenzene is then allowed to enter. At first water, aniline, and nitrobenzene distil over, and are pumped back into the still. The rest of the iron is added by degrees, and, when the violence of the reaction has subsided, steam is again turned in. The aniline is thus distilled over without the addition of a base (*e.g.*, lime), which was formerly necessary when excess of acid was used. An ordinary charge consists of about 2,688 lbs. of borings ("swarf," the scrapings of soft castings), 2,350 lbs. of nitrobenzene, and 115 lbs. of hydrochloric acid. The reduction should not be conducted rapidly, or with excess of iron, as the aniline may be converted under such conditions into benzene and ammonia. The distilled aniline subsides to the bottom of the receiving tank, and is drawn off and rectified, the little that remains in the water being recovered by using this to feed the boilers supplying steam to the still in which the nitrobenzene is reduced.

Aniline, when pure, is a colourless oily liquid (the commercial product is generally brown), of specific gravity 1·027, and boiling

at 185° C. = 365° F. Aniline of good quality does not contain more than 0·5 per cent. of water. There are several grades of commercial aniline ("aniline oil") used in making aniline dyes. Thus, there are the grades "pure aniline oil" ("aniline for blue"), "aniline for red" and "toluidine." The first is nearly pure aniline; the second consists of a mixture of aniline, orthotoluidine and paratoluidine; the third is a mixture of orthotoluidine and paratoluidine (the latter amounting to about 35 per cent. of the whole). Aniline hydrochloride is known commercially as aniline salt. These bases, as well as xylidine, are made by methods similar in principle to that described for aniline.

All triphenylmethane derivatives are obtained by the elimination of hydrogen from phenyl derivatives, in the presence of some methane derivative, which may take the form of a methyl group in one of the phenyl derivatives, or may be brought into play in the form of a simple methane derivative. Thus, triphenylmethane itself was originally prepared by heating benzylidene chloride with mercury diphenyl, thus—

$$C_6H_5CHCl_2 + (C_6H_5)_2Hg = HC\begin{cases}C_6H_5\\C_6H_5\\C_6H_5\end{cases} + HgCl_2$$

In this case it will be noted that the chlorine and mercury both occupy the place of hydrogen, and that their mutual elimination is, therefore, chemically equivalent to the elimination of hydrogen. The other typical method, involving the use of a simple methane derivative, is exemplified by the reaction (in presence of aluminium chloride)—

$$3C_6H_6 + CHCl_3 = HC\begin{cases}C_6H_5\\C_6H_5\\C_6H_5\end{cases} + 3HCl$$

an actual elimination of hydrogen, as HCl, taking place.

Since triphenylmethane does not contain a chromophore, it is not a chromogen. Its amido-derivatives, which, as stated above, are capable of becoming chromogens, are prepared by methods analogous to those already mentioned, the amido-derivatives of benzene and its homologues forming the raw materials. Thus, pararosaniline base is prepared by eliminating hydrogen from a mixture of aniline and toluidine by oxidation. In this case, the methyl group of the toluidine affords the methane carbon atom round which the amidophenyl groups are disposed, thus—

$$2C_6H_5(NH_2) + C_6H_4\begin{cases}CH_3\\NH_2\end{cases} + O_3 = HO-C\begin{cases}C_6H_4(NH_2)\\C_6H_4(NH_2)\\C_6H_4(NH_2)\end{cases} + 2H_2O$$

Of the six hydrogen atoms eliminated by the action of the three oxygen atoms, two have been left, together with one oxygen

atom, as essential parts of the pararosaniline base (the relation of which to pararosaniline has been already given). The method of oxidation employed is similar to that used in the case of the production of rosaniline (**magenta**; **fuchsine**). Pararosaniline base is only used in the production of "aniline blue" (*v.i.*).

Magenta, the commonest aniline colour, is obtained by a reaction similar to that expressed by the above equation, save that two molecules of toluidine and one molecule of aniline are the proportions of these bases. This alteration is necessary, because the rosaniline base contains an amidotolyl group in place of one of the amidophenyl groups, thus—

$$C_6H_5(NH_2) + 2C_6H_4\begin{<}{CH_3}{NH_2} + O_3 = HOC\begin{<}{C_6H_3(CH_3)(NH_2)}{C_6H_4(NH_2)}{C_6H_4(NH_2)} + 2H_2O$$

The treatment of the rosaniline base with an acid induces the formation of the chromophoric group, eliminates water and forms the rosaniline salt—*e.g.*,

$$C\begin{<}{C_6H_3(CH_3)=\overset{H\ Cl}{\overset{\diagdown\ \diagup}{N}}H}{C_6H_4(NH_2)}{C_6H_4(NH_2)}$$

The process is carried out in one of two ways, which differ merely in the nature of the oxidising agent used. The older process consists in heating about 500 kilos. of "aniline for red" with 750 kilos. of arsenic acid solution containing 60 to 70 per cent. of H_3AsO_4, in iron pots, the temperature being slowly raised to 180° C. = 356°F., and the contents of the pots well stirred. The heating is continued until a sample is found to be brittle on cooling. Only about two-thirds of the bases in the aniline for red is converted into rosaniline by this process, the remainder distilling over and being worked up with the next batch. The melt containing rosaniline arsenite and arsenate and arsenious acid, formed by the reduction of arsenic acid, is broken up and boiled out with water, sodium chloride and hydrochloric acid being added to the liquor; rosaniline hydrochloride is precipitated and is recrystallised from brine. Various other colouring matters are produced in minor amount, and are recovered from the mother liquor. One of the chief is **chrysaniline** ($C_{19}H_{15}N_3$), the hydrochloride of which is known in the pure state as **phosphine**, a dyestuff used for leather and silk. The arsenious and arsenic acids are recovered by evaporating the liquors and burning the residue with the waste organic (tarry) matter of the process. By this means the arsenic is liberated as As. Its vapour is mixed with air and burnt to arsenious oxide in another chamber. This is converted into arsenic acid by nitric acid, the

nitrous fumes from the oxidation being re-oxidised to nitric acid by air in presence of water. Thus nitric acid and arsenic acid serve as carriers of oxygen from the air to the aniline and toluidine to be condensed for the production of rosaniline. Magenta obtained by this process is rarely free from arsenic. Legislative enactments in most countries have enforced the absence of arsenic from pigments and dyestuffs, and in consequence nitrobenzene is now largely used as an oxidising agent in place of arsenic acid. Aniline for red (100 parts) and nitrobenzene (40 parts) are heated with a small quantity of ferrous chloride to about 175° C. = 347° F., care being taken not to exceed this temperature. The reaction must not be pushed too far, and the mass on cooling should still contain some aniline and be consequently soft. This aniline is extracted by dilute hydrochloric acid, and the main mass containing rosaniline is worked up as in the case of that produced by the arsenic method. In the nitrobenzene process, the ferrous chloride acts as a carrier of oxygen to the aniline. It is doubtful whether the nitrobenzene acts in any way other than as an oxidant, for it appears that it does not yield aniline as a product, or, if it does, that this aniline remains as such at the end of the reaction, necessitating the extraction with hydrochloric acid already spoken of. The dyestuff obtained differs in no great degree from that prepared by the arsenic acid process, but is of course free from traces of arsenic, and thus meets legislative requirements. The yield, especially of the best grade of magenta (*q.v.*), is, however, slightly higher. The total yield is about 33 per cent. of the bases used. The bye-product characteristic of this method is the **induline** ($C_{24}H_{18}N_4$) in place of the chrysaniline of the arsenic acid process. Obviously, the cost of this process varies more greatly with the price of benzene than does that of the arsenic method of preparation.

Magenta, as at present met with in the market, is rosaniline hydrochloride, $C_{20}H_{19}N_3, HCl, 4H_2O$, the manufacture of the acetate and nitrate being obsolete. It crystallises in octahedra or rhombic tables of green lustre, difficultly soluble in cold water. It dyes silk and wool directly from its aqueous solution, and cotton with a tannin mordant. It is brilliant, but not fast to light. When it is required to dye with magenta from an acid dye-bath, the sodium salt of the disulphonic acid, $C_{20}H_{17}N_3(SO_3Na)_2$, is prepared by heating rosaniline hydrochloride with fuming sulphuric acid at 150° C. = 302° F., the usual practice of neutralising with chalk and forming the sodium salt by the action of sodium carbonate on the calcium salt (see *Alizarins*, p. 281) being adopted. The substance thus prepared (**acid magenta**) is a metallic looking powder easily soluble in water; it is used for dyeing wool and silk. **Magenta base** (rosaniline base), $C_{20}H_{21}N_3O$, is prepared by precipitating the hydrochloride with lime or ammonia. It

separates from the filtered liquid in crystals, which are colourless when kept from contact with an acid, but speedily become pink on exposure to air from absorption of CO_2. It is sometimes used for the production of the sulphonate described above, and of other colours (*v.i.*).

Other aniline dyestuffs (blue and violet in colour) are derivatives of rosaniline or pararosaniline, containing paraffin or aromatic radicles in place of the hydrogen in the amido-groups. The typical method originally used for preparing them consists in treating rosaniline with a halogen substitution product of methane or ethane—*e.g.*, CH_3Cl or C_2H_5I—the hydrogen of the amido-groups of the rosaniline being thus replaced by a paraffin radicle. In modern practice it is found preferable to convert substituted anilines into corresponding substituted rosanilines, instead of using the substitution process given above. Thus, in the preparation of **methyl violet** (a mixture of tetramethyl-, pentamethyl- and hexamethylpararosaniline), dimethylaniline is prepared by heating aniline with excess of methyl alcohol and hydrochloric acid, or sulphuric acid, in enamelled iron digesters at a temperature of 180° to 200° C. = 356° to 392° F. The base is liberated with lime, distilled, and freed from monomethylaniline and aniline by freezing artificially. The dimethylaniline, $C_6H_5{\cdot}N(CH_3)_2$, is heated in a current of air with cupric chloride (from sulphate of copper and common salt), which behaves as an oxidising agent, the cuprous chloride produced acting as a carrier of oxygen (*cf. Deacon's Chlorine Process*, p. 39). Phenol is commonly added, but its function is not clear. The double cuprous chloride of methyl violet is treated with ferric chloride, cupric chloride and ferrous chloride being thus formed, and the hydrochloride of the methyl violet is salted out in the usual way; the yield is nearly that indicated by theory. The commercial salt occurs in amorphous masses of green lustre, giving violet solutions which become bluer the further the substitution of methyl groups for hydrogen has been pushed. As in the case of magenta, sulphonated derivatives are sometimes prepared, the method adopted consisting in reduction to the leuco-compound,* sulphonation (p. 288), and subsequent oxidation. This order of treatment is made requisite by the difficulty of directly sulphonating methyl violet. Methyl violet dyes silk and wool directly, and cotton with a tannin mordant.

The pure hexamethylpararosaniline constitutes another dyestuff of this class, and is known as **crystal violet**. It is prepared by the action of carbonyl chloride on dimethylaniline in presence of zinc or aluminium chloride, the reaction proceeding in two stages, thus—

* The term "leuco-compound" is commonly applied to the product of the reduction of organic dyestuffs by means of the action of zinc in acid or alkaline solution ("nascent hydrogen").

(1) $2C_6H_5\cdot N(CH_3)_2 + COCl_2 = CO\langle^{C_6H_4\cdot N(CH_3)_2}_{C_6H_4\cdot N(CH_3)_2} + 2HCl$

Tetramethyldiamidobenzophenone.

(2) $CO\langle^{C_6H_4\cdot N(CH_3)_2}_{C_6H_4\cdot N(CH_3)_2} + C_6H_5\cdot N(CH_3)_2 = HO-C\langle^{C_6H_4N(CH_3)_2}_{C_6H_4N(CH_3)_2}_{C_6H_4N(CH_3)_2}$

Hexamethylpararosaniline base.

The commercial salt is the hydrochloride, and is used in the same way as magenta.

The aniline blues are examples of substituted rosanilines containing an aromatic radicle. When aniline is heated with rosaniline no reaction occurs, unless an organic acid be present (benzoic acid for choice); a very small proportion is requisite to induce their interaction. The aniline used is pure ("aniline for blue") in order to avoid the red tones produced by higher bases. The highest substitution product that can be formed in this manner is triphenylrosaniline, $C_{20}H_{16}(C_6H_5)_3N_3$, which has the bluest shade of the phenyl derivatives. To ensure its production a considerable excess of aniline is needed. The method of manufacture consists in heating rosaniline base (50 parts), aniline (300 parts) and benzoic acid (3 parts) to 180° C. = 356° F. The melt is partly neutralised with hydrochloric acid, and the hydrochloride of triphenylrosaniline crystallises. The aniline blue thus obtained is but little soluble in water, but fairly easily soluble in alcohol, whence its name "spirit blue." It is chiefly used for the preparation of sulphonated derivatives, which are readily formed by the action even of vitriol instead of fuming sulphuric acid, the sodium salts being known by the names of "alkali blue" * and "soluble blues," and being used for dyeing cotton, wool and silk.

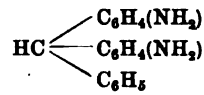
A class of dyestuffs related both to the aniline violets (in their mode of preparation) and to the aniline blues, in respect of the fact that they are aromatic derivatives, may be mentioned here. They include Victoria blue and night blue, and are diphenylnaphthylmethane derivatives. By the action of $COCl_2$ on dimethylaniline, as in the preparation of the aniline violets, tetramethyldiamidobenzophenone is produced. This is heated with a dehydrating agent and phenyl-α-naphthylamine, yielding bodies of the form

$$C\langle^{C_6H_4\cdot N(CH_3)_2}_{C_6H_4\cdot N(CH_3)_2}_{C_{10}H_6=N(C_6H_5)}\quad H\ Cl$$

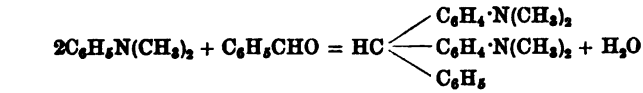
* This can be used in an alkaline bath, hence its name.

These blues dye silk and wool from an acid bath, and cotton with an alumina and oil mordant.

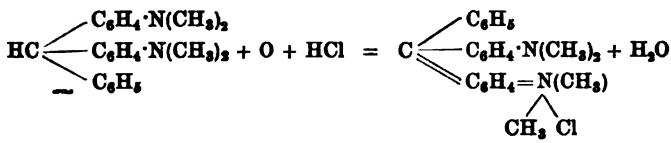
The foregoing dyestuffs contain three amido- or substituted amido-groups. Another series of dyestuffs is derived from diamidotriphenylmethane—



The principal dyestuff of this class (**malachite green** or **benzaldehyde green**) is prepared by heating a mixture of benzaldehyde and dimethylaniline with hydrochloric acid, whereby water is eliminated, thus—

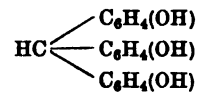


The leucomalachite green thus produced is then dissolved in hydrochloric acid, and oxidised by the addition of PbO_2, thus—

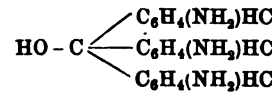


The lead, which remains in solution as chloride, is precipitated by means of sodium sulphate, and the dyestuff is salted out with zinc chloride, with which it forms a double salt constituting the commercial product. The oxalate is also prepared. Malachite green forms green crystals of metallic lustre, readily soluble in water, dyeing wool and silk directly, and cotton with a tannin mordant. It is not a particularly fast colour.

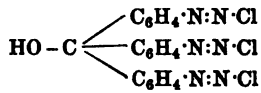
Aurine dyestuffs are triphenylmethane derivatives containing phenolic hydroxyl groups, the parent substance being trihydroxytriphenylmethane,



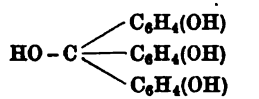
A method of synthesis of theoretical interest consists in converting pararosaniline hydrochloride into triamidotriphenylcarbinol trihydrochloride,



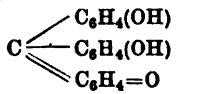
by the action of hydrochloric acid and water. By treating this with nitrous acid it is diazotised (p. 274) into



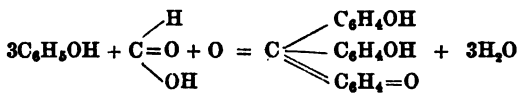
which, on hydrolysis, is converted into trihydroxytriphenylcarbinol,



this body at once loses water, and becomes the corresponding inner anhydride (aurine),

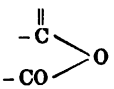


The actual members of this class of dyestuffs are substituted-aurines. The commercial product called "aurine" is prepared by heating 3 parts of phenol with 2 of anhydrous oxalic acid (potential formic acid) and 1·5 of strong sulphuric acid, to a temperature of 120° to 130° C. = 248° to 266° F.—



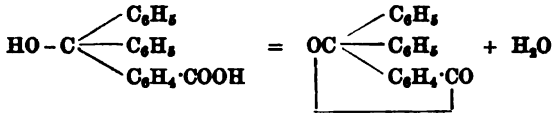
The formic acid represented above is a product of the breaking down of the oxalic acid; the source of the extra oxygen required is not definitely known, but it is probably the air. The melt is extracted with water, the product being a green lustrous substance, becoming brown on powdering. The commercial product obtained in this way is termed yellow coralline, and consists of a mixture of aurine, rosolic acid—its methyl derivative—and other colouring matters. By the action of ammonia, in alcoholic solution, upon coralline, a mixture of substances (called peonine) intermediate between aurine and rosolic acid on the one hand, and pararosaniline and rosaniline on the other, is obtained. Coralline is not a fast colour, and is chiefly used for colouring wall paper, and as an indicator.

Phthalein dyestuffs are a class of triphenylmethane derivatives, of which the chromophore is the lactone ring—



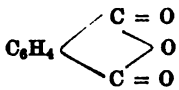
They may be regarded as substitution products from phthalo-

phenone which is the inner anhydride (lactone) of triphenylmethanecarbinolorthocarboxylic acid :—



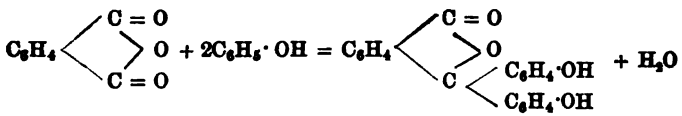
Triphenylmethanecarbinolorthocarboxylic acid. Phthalophenone.

They are obtained by the use of phthalic anhydride.*

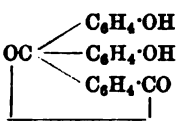


When this compound is heated with phenols (the OH groups of which act as auxochromes in the final product), water is eliminated, and two ring nuclei replace one of the carbonyl oxygen atoms, as will be seen in the following case :—

By heating phthalic anhydride with phenol in the presence of a dehydrating agent (*e.g.*, $ZnCl_2$), the following reaction occurs:—



The body thus formed may also be represented as dihydroxyphthalophenone—



This compound (**phenolphthalein**) — which is a pale yellow crystalline substance, sparingly soluble in water, but freely in alcohol—yields derivatives in which the phenol hydrogen is replaced by an alkali metal; these are bright red and are decomposed by the feeblest acids (*e.g.*, CO_2), so that phenolphthalein is useless as a dyestuff, but valuable as an indicator.

Fluorescein is obtained when resorcinol (metadihydroxybenzene), $C_6H_4(OH)_2$, is substituted for phenol in the above reaction.

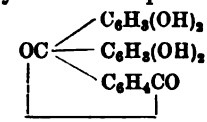
*Phthalic anhydride is prepared from naphthalene tetrachloride, $C_{10}H_8Cl_4$, which is made by adding a mixture of naphthalene with twice its weight of potassium chlorate to hydrochloric acid. The tetrachloride separates in crystals, and is washed and oxidised to phthalic acid by boiling nitric acid (specific gravity 1·4). The nitric acid is evaporated and the residue is distilled, the phthalic acid being dehydrated and becoming phthalic anhydride at the temperature of the distillation. Phthalic anhydride crystallises in long flexible colourless needles, melts at 128° C. = 262° F., boils at 284° C. = 543° F., and becomes converted into the acid when boiled with water.

The resorcinol for the manufacture of this dyestuff is prepared by fusing benzene metadisulphonic acid with caustic soda. The sulphonic acid is made by heating benzene (free from thiophen) with strong sulphuric acid, which first yields the monosulphonic acid; on heating this, dissolved in the excess of sulphuric acid originally taken, with sodium sulphate in order to allow of a high temperature (225° C. = 437° F.) being obtained (by the formation of $NaHSO_4$), the disulphonic acid is produced; it is converted by the usual methods into the sodium salt (p. 281), and this is added to fused caustic soda, with which it reacts thus :—

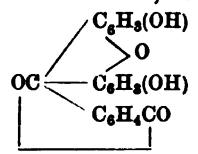
$$C_6H_4(SO_3Na)_2 + 4NaOH = C_6H_4(ONa)_2 + 2Na_2SO_3 + 2H_2O$$

The sodium resorcinol is dissolved in water, the solution made acid with hydrochloric acid, and the liberated resorcinol extracted with amyl alcohol, which is afterwards separated by distillation, leaving crude resorcinol which is purified by distillation under diminished pressure. Resorcinol crystallises in colourless needles and prisms, melts at 119° C. = 246° F., and boils at 276° C. = 529° F.

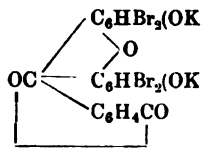
The reaction obtained on heating a mixture of resorcinol and phthalic anhydride takes place in a manner similar to that described above for phenolphthalein. No dehydrating agent (*e.g.*, $ZnCl_2$) is necessary. The first product is **resorcinolphthalein**,



which then loses a molecule of water, becoming **fluorescein**,



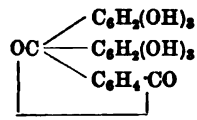
Fluorescein, as generally prepared, occurs only as a brown crystalline powder, insoluble in water but soluble in alcohol to a brown solution, showing, particularly when dilute, a green fluorescence. It is too sensitive to light to be used as a dyestuff; its halogen derivatives, on the other hand, are thus employed. Such are the **eosins**, alkali salts of halogen substitution products of fluorescein. Ordinary or "soluble" eosin is the potassium salt of tetrabromofluorescein,



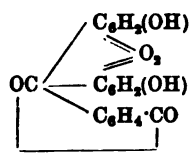
It is prepared either by direct bromination of fluorescein suspended in alcohol, or by preparing a mixture of sodium bromide and bromate, by dissolving bromine in caustic soda and heating the solution (to decompose hypobromite), mixing this solution with one of fluorescein in caustic soda and acidifying the cooled mixture. The acid liberates bromine by the interaction of hydrobromic acid and bromic acid, and effects the bromination of the fluorescein which, being insoluble in the aqueous liquid, is precipitated. It is dissolved in potassium carbonate solution, and the potassium salt is thus formed. Eosin forms reddish crystals, highly fluorescent in dilute solution. It is not a fast dye, though better in this respect than fluorescein, but is used for wool and silk in an acid bath on account of the brilliant red shade which it yields. It is much used for red inks and for preparing lake pigments (*q.v.*).

Eosins soluble in spirit are also prepared by substituting the group CH_3 or C_2H_5 for one atom of K. The sodium salt of tetraiodofluorescein constitutes the dyestuff known as erythrosin. This substance is prepared by the direct action of iodine upon fluorescein in presence of an oxidising agent, which incidentally secures economy of iodine, the hydrogen iodide formed by metalepsis * being oxidised to iodine, which is available for further reaction. The product is used to some extent as a dyestuff, as an indicator and for making orthochromatic photographic dry plates. By the substitution of two NO_2 groups for two of the bromine groups in ordinary eosin, eosin scarlet or safrosin can be prepared.

By substituting pyrogallol, $C_6H_3(OH)_3$, for resorcinol in the reaction with phthalic anhydride, gallein is obtained instead of fluorescein. (Both this and similar derivatives of phenols containing more than two (OH) groups, yield darker colours than those of the dyestuffs from phenol and resorcinol.) The primary product is pyrogallolphthalein,

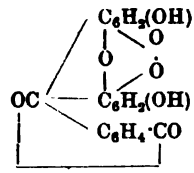


which, losing two molecules of water, becomes



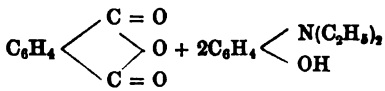
* Metalepsis is a convenient term for the class of reaction typified by the removal of hydrogen by a halogen, as its hydrogen compound, and the simultaneous substitution of the halogen.

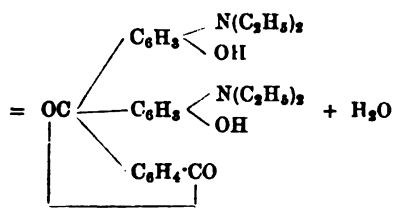
and then, by oxidation by air, **gallein**—



In the manufacture of the dyestuff, gallic acid, $C_6H_2(OH)_3COOH$, may be used instead of pyrogallol, as on heating it is converted into that body, CO_2 being eliminated. Commercial gallein is a violet paste, dissolving in alkalies with the production of a blue colour. It dyes chrome-mordanted wool a dark violet. **Cœrulein** is prepared from gallein by heating the latter with 20 times its weight of strong sulphuric acid at 200° C. = 392° F. Its empirical formula is $C_{20}H_8O_6$, being gallein minus a molecule of water. Its structure is not definitely known, but it is believed to be an anthraquinone derivative, whence its alternative names **anthracene green** and **alizarin green**. In its commercial form it is a black paste soluble in alkalies; it is much used for dyeing wool and cotton, especially in calico-printing. It yields a fast olive-green colour with various mordants. A soluble form of cœrulein is the sodium bisulphite compound, $C_{20}H_8O_6.2NaHSO_3$.

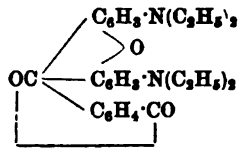
The foregoing phthalein compounds are of an acid character, owing to the presence of phenolic hydroxyl groups. When these are replaced by amido-groups, basic dyestuffs are formed. The simplest method of attaining this end would be, for example, to use metamidophenol, $C_6H_4(OH)(NH)_2$, instead of resorcinol, as the compound to be heated with phthalic anhydride. The substance thus produced is of no practical value, but on using diethylmetamidophenol the dyestuff known as **rhodamine** is produced, thus—





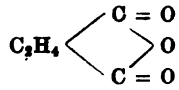
Diethylamidophenolphthalein.

This body, losing water, becomes rhodamine,



The commercial product is the hydrochloride of the base, and is obtained as a red powder soluble in water to a red fluorescent solution. It dyes silk and wool directly, and cotton with a tannic acid mordant. The colour is fairly fast.

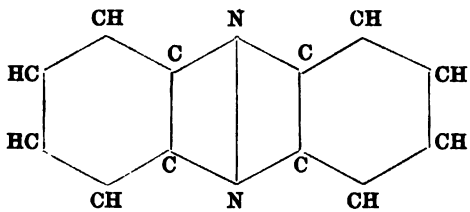
A dyestuff known as rhodamine S is a condensation product of diethylmetamidophenol with succinic anhydride



in place of phthalic anhydride. It is not, therefore, a triphenylmethane derivative. It is very similar to rhodamine itself in its dyeing properties.

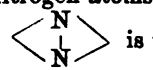
(*e*) **Azine Compounds.**—The characteristic grouping which distinguishes these compounds is

R″ is a divalent radicle, such as $(C_6H_4)''$, or its substituted product $(C_6H_3 \cdot CH_3)''$. Thus, the simplest body of this class will be



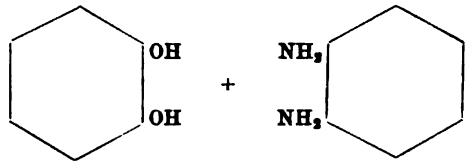
Diphenylene azine or phenazine.

The nitrogen ring is thus seen to be attached to adjacent C atoms; the nitrogen atoms are therefore in the ortho position.

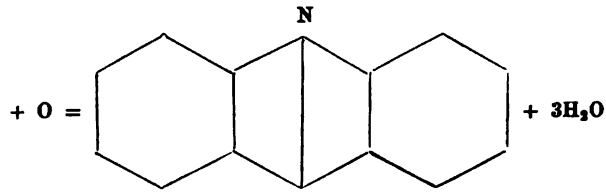
The group  is the chromophore of these bodies, but they become dyestuffs only on the introduction of the auxochrome NH_2 or OH.

An example of the formation of an azine is furnished by the

reaction between a dihydroxy-derivative and an ortho-diamine, in presence of oxygen, thus :—



Pyrocatechol (Orthodihydroxybenzene). **Orthophenylenediamine.**



Phenazine.

A general method for preparing dyestuffs of azine type, consists in heating an orthoamidoazo-compound with a monamine. The reaction may be represented as proceeding in two stages :—

(1) $(NH_2)(CH_3)C_6H_3 \cdot N : N \cdot C_6H_3(CH_3)(NH_2) + H_4$

Orthoamidoazotoluene.

$= 2C_6H_3(CH_3)(NH_2)_2$

Orthotoluylenediamine.

(2) $C_6H_3(CH_3)(NH_2)_2 + C_{10}H_7(NH_2)$

α-Naphthylamine.

$= (CH_3)C_6H_3 \langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle C_{10}H_5(NH_2) + H_6$

Eurhodine (amidotolunaphthazine).

It is obvious that the elimination of H in the second part of the reaction more than balances the absorption of H in the first. Thus, the reaction can proceed without the introduction of an external reducing agent. The use of an excess of the azo-compound serves to absorb the excess of hydrogen after the above equations are satisfied. The actual method of production consists in heating orthoamidoazotoluene with α-naphthylamine hydrochloride, dissolved in phenol, at 130° C. = 266° F. When the melt has become scarlet, the hydrochloride of the eurhodine is precipitated by the addition of toluene. Treatment of the hydrochloride with an alkali yields the free base, which forms yellow prisms or brown needles. Since the salts of eurhodine are decomposed by an excess of water they are not adapted for

use as dyestuffs, the scarlet shade which they impart to fabrics being bleached by water to the yellow of the free base.

Another dye of this class, but distinguished by containing two amido-groups (one of which contains two methyl radicles) is **toluylene red**, which may be formed thus—

$$C_6H_4(NH_2)[N(CH_3)_2] + C_7H_6(NH_2)_2 + O_2$$

Dimethylparaphenylenediamine. Metatoluylenediamine.

$$= [N(CH_3)_2]C_6H_3 \langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle C_7H_5(NH_2) + 3H_2O.$$

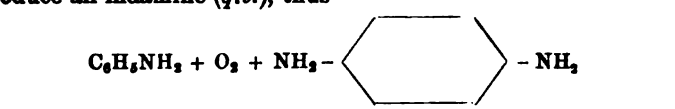
Toluylene red.

This dyestuff is also obtained as a decomposition product on heating toluylene blue (p. 303). It dyes cotton with a tannin mordant.

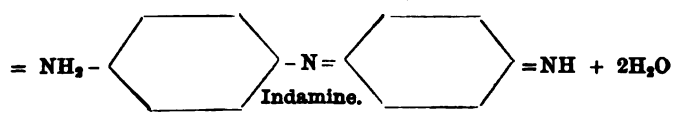
It will be seen that the eurhodines are amido-derivatives of azines. By hydrolysis (heating with strong hydrochloric acid under pressure) the amido-group is replaced by hydroxyl, the corresponding **eurhodol** being the product. The typical compound of the class is **hydroxytolunaphthazine**. It is prepared from eurhodine in the manner indicated above. As in the case of all azines, the $\langle \begin{matrix} N \\ | \\ N \end{matrix} \rangle$ group has basic properties, so that the eurhodols, which contain also phenolic hydroxyl, behave as both acid and basic compounds.

Most of the basic dyestuffs hitherto dealt with are referable to ammonia as a type. The **safranines**, about to be spoken of, are, on the contrary, complex ammoniums, and are called **azonium bases**, since they resemble the azines in structure, save that one of the chromophoric nitrogen atoms has become pentatomic and therefore capable of fixing a monovalent positive radicle and a monovalent salt-forming element or radicle (*e.g.*, Cl).

The general mode of preparation of these substances may be typified by the oxidation of a mixture of one molecule of a paradiamine, such as paraphenylenediamine, with two molecules of a monamine (as a salt—*e.g.*, the hydrochloride), such as aniline. The first stage of the reaction takes place between the diamine, oxygen and one of the molecules of the monamine, to produce an indamine (*q.v.*), thus—

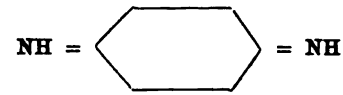


Paraphenylenediamine.

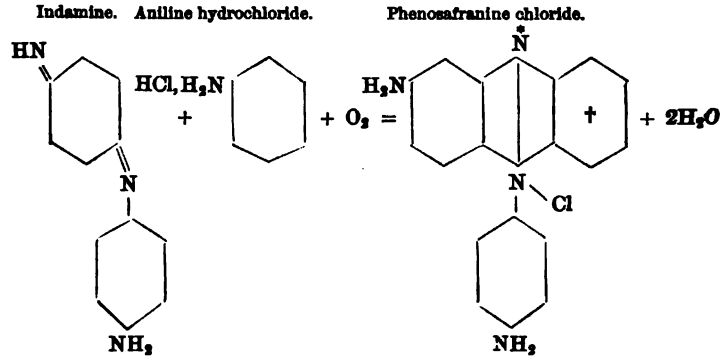


Indamine.

It would seem that paraphenylene diamine first becomes quinone di-imide



i.e., quinone with (NH)″ in place of the O of the quinone C = O groups, and that this then undergoes condensation with the aniline. In the second stage of the reaction, the indamine and the second molecule of aniline (as hydrochloride) undergo a further condensation and oxidation, hydrogen being again removed as water.

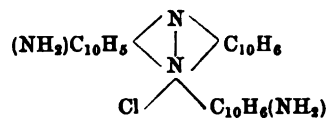


The chlorides of the safranines are red, and become blue in the presence of strong hydrochloric acid and green in that of strong sulphuric acid, from the formation of a diacid and a triacid salt respectively. On dilution with water the acid salts are decomposed, and the red colour is restored. **Phenosafranine** is prepared by the reaction given above; the hydrochlorides of the bases employed being dissolved in hot water and oxidised by potassium bichromate or manganese dioxide. The first stage (the formation of the indamine) is indicated by the appearance of a blue colour, which speedily gives place to the red of phenosafranine. The chromium or manganese oxide and less basic dyestuffs present as impurities, are precipitated by caustic soda, the solution filtered and the dyestuff salted out, after the addition of hydrochloric acid. Phenosafranine dyes wool and silk directly, whilst cotton requires a tannin mordant. The corresponding body, **tolusafranine** (**safranine T**), is also a red dyestuff, capable of dyeing wool in an alkaline bath, and having a slight attraction for cotton fibres; a mordant is, however, necessary for the production of a fast colour.

* This is taken to be the nitrogen of the aniline.
† This is the aniline ring.

Naphthalene red (Magdala red) is another dyestuff of this class made by reactions similar to those used for phenosafranine, but has naphthalene rings in place of the benzene rings of the last-named dyestuff. It can be produced by heating naphthylenediamine with α-naphthylamine and an oxidising agent, an indamine being formed as an intermediate product, but this method is not practicable because of the great ease with which naphthylenediamine is oxidised to α-naphthoquinone. By substituting amidoazonaphthalene, $(NH_2)C_{10}H_5 \cdot N:N \cdot C_{10}H_6(NH_2)$, for naphthylenediamine the use of an oxidising agent can be avoided, inasmuch as amidoazonaphthalene is readily reduced to naphthylenediamine, $C_{10}H_6(NH_2)_2$ (*cf.* formation of eurhodine given above). According to modern practice a mixture of 23 kilos. of naphthylenediamine hydrochloride, 26 kilos. of α-naphthylamine and 59 kilos. of amidoazonaphthalene is heated at 130° to 140° C. = 266° to 284° F. until the blue colour of the mixture (due to the indamine first formed) becomes red. The function of the naphthylenediamine is to form some Magdala red (with the α-naphthylamine) with the elimination of hydrogen, which then reduces the amidoazonaphthalene to naphthylenediamine, the latter continuing the cycle of reactions.

Naphthalene red * has the formula

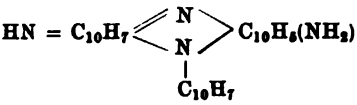


and occurs as a dark brown powder sparingly soluble in hot water. It is only used in silk dyeing (imparting a pink fluorescent colour) as it is a costly material.

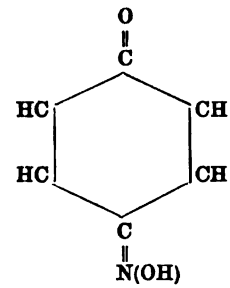
Mauveine has the empirical formula $C_{27}H_{25}N_4$, and appears to be a phenyl safranine. Recently it has been classed with the indulines (*q.v.*). It is made by the oxidation of aniline oil containing toluidine, by bichromate of potash and sulphuric acid. A black mass is obtained from which the mauve may be extracted by water. It was the first dyestuff obtained from aniline. It is sold as a violet paste and dyes silk and wool directly.

Among the minor classes (not provided for in the classification given at the head of this section) of synthetic organic colouring matters, the following groups and individuals may be mentioned.

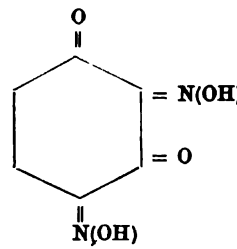
* Recent investigations seem to show that naphthalene red is an induline (p. 312) dyestuff—



Quinonoximes.—The simplest quinonoxime has the formula

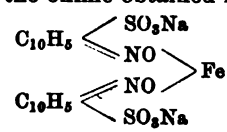


It is sometimes regarded as nitrosophenol, $C_6H_4(NO)(OH)$. This substance is not used as a dyestuff, but the corresponding body derived from resorcinol, $C_6H_4(OH)_2$, viz.—"**quinonedioxime**" or dinitrosoresorcinol



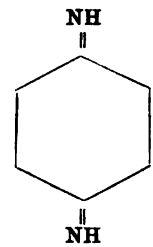
is thus used, and is made by adding sulphuric acid to an aqueous solution of resorcinol and sodium nitrite. The commercial dyestuff, known as **resorcin green** or **solid green**, occurs as yellowish-brown or green plates, or as a brownish powder. It is sparingly soluble in cold water and acts as an acid dyestuff. It is used for dyeing cotton on an iron mordant, the dye produced being green. Another dyestuff derived from resorcinol is **lacmoid**, $C_{12}H_9NO_4$, the constitution of which is not definitely known. It is a dark violet substance, used as an indicator. It is made by heating 100 parts of resorcinol with 5 of sodium nitrite and 5 of water at 120° C. = 248° F.

Naphthoquinoximes, $O = C_{10}H_6 = NOH$.—Two isomerides exist; they are obtained by treating the corresponding naphthols with nitrous acid, and are sold under the names of **gambine R** and **gambine Y**. They are used in calico-printing, with iron mordants, and produce a green shade. The iron derivative of the sodium sulphonate of the oxime obtained from β-naphthol,

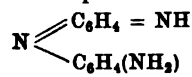


is sold as **naphthol green**. It is a dark green powder soluble in water, and dyes wool and silk directly.

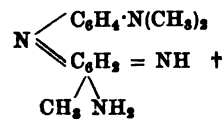
The derivatives of the chromophore quinonedi-imide,



obtained by the interaction of the dichloro-derivative of this compound, $C_6H_4(NCl)_2$,* with an aromatic amine, are called **indamines.** They are more conveniently obtained by the oxidation of a mixture of equal molecular proportions of an aromatic paradiamine and some other aromatic amine. The equation for this reaction for paraphenylenediamine and aniline has been given above (p. 299). The indamine produced

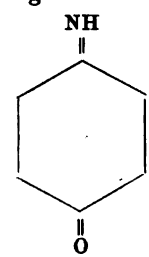


is known as **phenylene blue.** It is a basic body, and its salts are greenish-blue, dissolving in water. They are not largely used. **Toluylene blue** has a similar structure,



and is obtained by oxidising a mixture of dimethylparaphenylenediamine and metatoluylenediamine. The dyestuff is generally prepared as the hydrochloride. It is very soluble in water. When heated it yields toluylene red (p. 299).

The **indophenols** may be regarded as derivatives of quinoneimide,



* Obtained by the action of bleaching powder solution on paraphenylenediamine hydrochloride.

† The relation to quinone di-imide is indicated by the presence of two doubly-linked N atoms.

so that they differ from the indamines in that the $(NH)''$ group is replaced by a doubly-linked oxygen atom. They are obtained by substituting phenols for amines in the method already given for preparing indamines. Thus, the oxidation of equal molecular proportions of paraphenylenediamine and phenol gives indophenol, the equation being

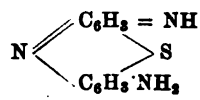
$$C_6H_4(NH_2)_2 + C_6H_5OH + O_2 = O{=}C_6H_4{=}NC_6H_4NH_2 + 2H_2O.$$

This typical indophenol is of no practical importance. The dimethyl derivative (phenol blue), a greenish-blue substance, is used as a dyestuff.

Naphthindophenol,* $O = C_{10}H_6 = NC_6H_4[N(CH_3)_2]$, is the most important of this class of dyestuffs; it is known as naphthol blue, and is prepared by oxidising an alkaline mixture of dimethylparaphenylenediamine and α-naphthol by means of air or bleaching powder. It is a dark blue powder with a coppery lustre, resembling indigo, for which it is much used as a substitute. It will be seen that the indophenols have no (OH) group, and are therefore not phenolic.

Their leuco-compounds, however, have a phenolic function and are soluble in alkalies, and from the solutions the indophenols are precipitated by oxidising agents, again recalling the behaviour of indigo. It follows from this that these dyestuffs can be applied in the reduced soluble state, and then oxidised on the fibre, being, in fact, ingrain colours (see *Primuline*, p. 277).

Dyestuffs containing Sulphur as an Essential Constituent.—One of these (primuline) has already been considered; its constitution is not sufficiently settled to bring it into this group, the dyestuffs in which are related to the indamines. This connection is evident from the formula for thionine, viz. :—



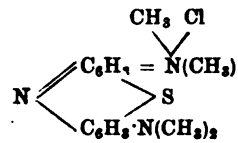
Compare that for phenylene blue (p. 303).

On comparison of this with the formula for the azine dyes, it will be seen that these derivatives may also be regarded as "thiazines" (better termed sulphazines; also termed thiazimes) having the group

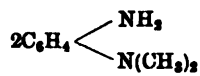
The chromophore is the same as in the indamine dyestuffs. The dyestuff, in the form usually prepared, is known as Lauth's violet, which is the hydrochloride of the base thionine. It is of no commercial importance.

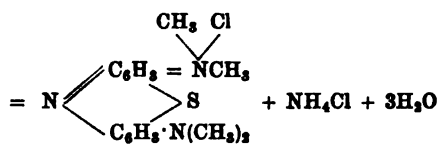
* Commercially known simply as indophenol.

Methylene blue is an ammonium base, but its structure is otherwise similar to that of thionine, being

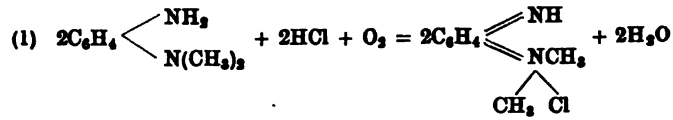


The principle underlying the methods of making this body is the oxidation of dimethylparaphenylenediamine in the presence of sulphur. For making this diamine, dimethyl aniline is treated with nitrous acid which converts it into nitrosodimethylaniline, and this compound is reduced either by zinc or sulphuretted hydrogen. In the older process, this dimethylparaphenylenediamine was treated with H_2S and ferric chloride in acid solution. The reaction may be represented thus (the ferric chloride acting as an oxidant)—

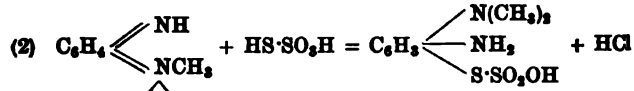




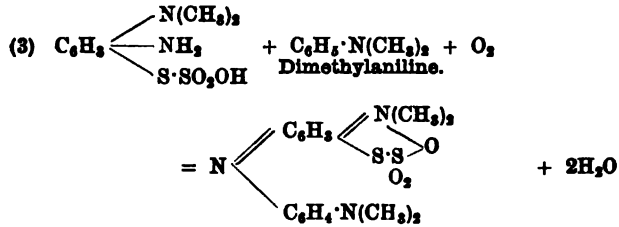
The methylene blue thus obtained is thrown out of solution by a mixture of salt and zinc chloride, a compound with zinc chloride being produced. According to modern practice the following process is preferred to that described above, as affording a better yield. It will be seen that whereas in the older process a portion of the dimethylparaphenylenediamine is broken up with the elimination of ammonium chloride, thus causing the consumption of the nitrogen of a costly substance for the production of one of relatively insignificant value, in the later method no such waste occurs. Dimethylparaphenylenediamine is oxidised, and the red product treated with sodium thiosulphate and an acid. The compound thus obtained, dimethylparaphenylenediamine "thiosulphonic" acid (*v.i.*), is mixed with dimethylaniline hydrochloride, and oxidised with a solution of potassium bichromate. A green crystalline indamine separates. This is boiled with a solution of zinc chloride, whereupon methylene blue is formed and crystallises as a double chloride. The chemistry of the process will be obvious from the following equations:—



Dimethylparaphenylene-diamine. Methylquinonediimide methochloride. (*Red oxidation product.*)

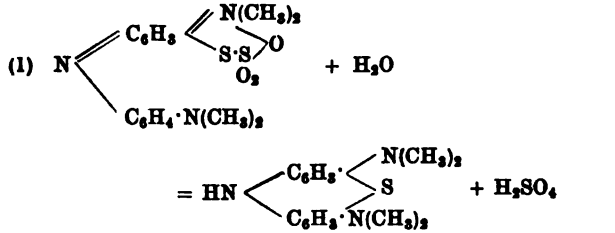


Dimethylparaphenylene-diamine sulphosulphonic acid.*

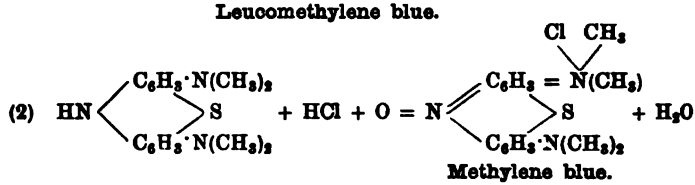


Tetramethylindamine sulphosulphonate. (*Green compound.*)

This compound on being boiled with zinc chloride solution in presence of iron is both hydrolysed and oxidised, the reactions being shown in the following stages—



Leucomethylene blue.



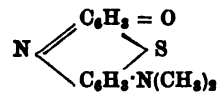
Methylene blue.

Methylene blue is easily soluble in water. Like ammonium

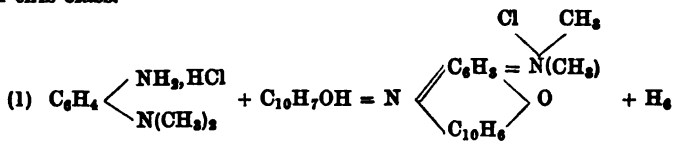
* Loosely termed thiosulphonic acid.

bases generally it is not a good dye for wool, but it finds considerable application for dyeing silk directly and cotton with a tannin mordant. It is faster to light than is Victoria blue—another basic blue dyestuff. It is of value as a stain for microscopic objects.

Methylene violet is prepared by treating dimethylpara-amidophenol with an oxidising agent in presence of sulphuretted hydrogen. Since the parent substance contains but one amido-group, methylene violet has the structure

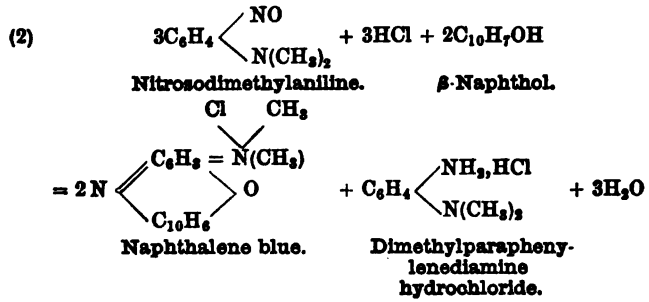


Oxazine colouring matters.—These compounds are analogous to the preceding, for they are similarly constituted save that oxygen replaces sulphur. They may also be prepared by methods similar to those employed for their sulphur congeners. Thus, paradiamines may be treated with phenols in presence of oxygen, which takes the place of the sulphur used in the process for the manufacture of the sulphurised dyes, and the phenol supplies the second ring nucleus, which, in the preparation of the sulphazines by the analogous process, is obtained at the expense of a second molecule of the paradiamine broken up by the oxidising agent employed. The preparation of **naphthalene blue** (*Meldola's blue*) will serve as a type of the reaction which produces compounds of this class.



Diamethylparaphenylenediamine. β-Naphthol. Naphthalene blue.

To induce the occurrence of this reaction an oxidising agent must be present, and this is conveniently furnished as nitrosodimethylaniline, which can itself take the place of paraphenylenediamine as a raw material, undergoing the change



Nitrosodimethylaniline. β-Naphthol. Naphthalene blue. Dimethylparaphenylenediamine hydrochloride.

It is obvious from a consideration of these two reactions that by the use of a somewhat larger proportion of nitrosodimethylaniline (acting as an oxidant) a portion of the dimethylparaphenylene-diamine produced in equation (2), can be caused to condense with another portion of β-naphthol in accordance with equation (1); the paraphenylene-diamine ultimately left (by equation (2)) will be smaller in quantity than that first appearing as a bye-product. By the extension of this principle waste can be reduced to a minimum. In practice, the raw materials (nitrosodimethylaniline and β-naphthol) are boiled together in alcoholic solution and the dyestuff precipitated by the addition of zinc chloride. The product is a bronze-violet powder, soluble in water to a deep violet solution, which dyes cotton mordanted with a tannin mordant to an indigo blue colour. When the free base of naphthalene blue, made by precipitating the dyestuff with an alkali, is heated, it undergoes condensation and molecular re-arrangement. The constitution of the colouring matter obtained, provisionally called a "cyanamine," requires further investigation; its empirical formula is $C_{26}H_{26}N_4O_2$.

Another important dye belonging to the oxazines is **gallocyanin** which is prepared by heating together nitrosodimethylaniline and gallic acid in aqueous solution, and precipitating the dyestuff by the addition of salt.

$$3C_6H_4\begin{cases}NO\\N(CH_3)_2\end{cases} + 2C_6H_2(OH)_3COOH$$

Gallic acid.

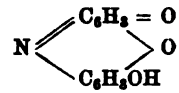
$$= 2N\begin{cases}C_6H_3\cdot N(CH_3)_2\\O\\C_6H(OH)\end{cases}\!\!<\begin{matrix}O\\COOH\end{matrix} + C_6H_4\begin{cases}NH_2\\N(CH_3)_2\end{cases} + 3H_2O$$

Gallocyanin.

Gallocyanin is a greenish paste dissolving in hydrochloric acid with a red colour, and in alkalies with a reddish-violet colour. The methyl salt, containing CH_3 in the place of H of the COOH group, is known as **prune**, and is bronze-colour in the solid state. These dyes are used in calico-printing on chromium mordants, with which they give violet shades.

One other class of oxazines includes the dyestuff **resorufin.** This is prepared by heating resorcinol with five times its weight of strong sulphuric acid, containing nitrous acid, at 100° C. = 212° F., and precipitating the colouring matter with water. In this process, nitrosoresorcinol is formed by the action of the nitrous acid on one part of the resorcinol, and this undergoes condensation with the remaining resorcinol, water being ab-

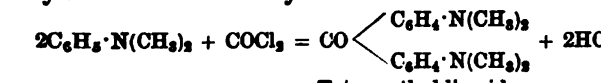
stracted by the sulphuric acid. The following formula represents the structure of resorufin :—



This substance is only coloured in neutral or alkaline solutions, which are not suitable as dye-baths. The commercial product is the tetrabromo-derivative (2 atoms of bromine in each ring), prepared by adding bromine to a solution of resorufin in potassium carbonate, and acidifying. It is sent into the market as the ammonium salt.

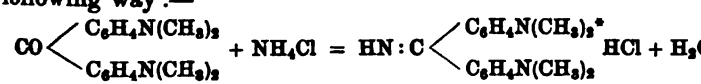
The chief remaining synthetic organic dyestuffs may be conveniently dealt with individually rather than in groups.

Auramine.—This compound is a ketoneimide, the chromophore being C = NH. It is prepared from tetramethyldiamidobenzophenone, the formation of which is carried out by acting on dimethylaniline with carbonyl chloride



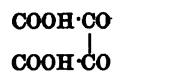
Tetramethyldiamido-benzophenone.

This latter body on being heated with a mixture of zinc chloride and ammonium chloride at 150° C. = 302° F. condenses in the following way :—

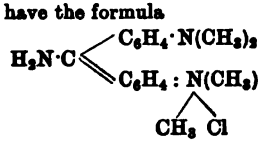


Commercial auramine is generally the hydrochloride, a yellow substance slightly soluble in cold water. It is one of the few basic yellow dyestuffs, and dyes silk and wool directly, and cotton mordanted with a tannin mordant.

Tartrazines.—These dyestuffs are the products of the reaction between phenylhydrazine and diketones. The best known, termed simply tartrazine, is prepared by acting on sodium dihydroxytartrate with sodium phenylhydrazine parasulphonate, in the presence of hydrochloric acid. Dihydroxytartaric acid may be regarded as derived from the diketone



* Recently, auramine has been classed with the diphenylmethane derivatives, and is alleged to have the formula



in which the two oxygen atoms have been replaced by four hydroxyl groups thus—

$$\begin{matrix}\mathrm{COOH{\cdot}C(OH)_2}\\ |\\ \mathrm{COOH{\cdot}C(OH)_2}\end{matrix}$$

Dihydroxytartaric acid.

The reaction between this body and phenylhydrazine may be represented as follows:—

$$\begin{matrix}\mathrm{COOH{\cdot}C(OH)_2}\\ |\\ \mathrm{COOH{\cdot}C(OH)_2}\end{matrix} + 2(\mathrm{H_2N{\cdot}NH{\cdot}C_6H_4SO_2ONa})$$

$$= \begin{matrix}\mathrm{COOH{\cdot}C = N{-}NH{\cdot}C_6H_4SO_2ONa}\\ |\\ \mathrm{COOH{\cdot}C = N{-}NH{\cdot}C_6H_4SO_2ONa}\end{matrix} + 4\mathrm{H_2O}$$

Compounds of this type are termed **osazones.**

Dihydroxytartaric acid may be prepared by the action of nitrous acid upon so-called **nitrotartaric acid,** obtained by the action of nitric acid upon tartaric acid.

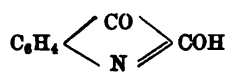
Phenylhydrazine is produced by reducing diazobenzene chloride, thus—

$$\mathrm{C_6H_5N : N{\cdot}Cl} + \mathrm{H_4} = \mathrm{C_6H_5HN{\cdot}NH_2{\cdot}HCl}$$

Diazobenzene chloride.	Phenylhydrazine hydrochloride.

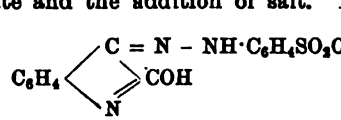
(The reducing agents used include stannous chloride, zinc and hydrochloric acid and sodium sulphite.) **Tartrazine,** the sodium salt of the above dicarboxylic acid, crystallises in yellow plates, soluble in water, and giving a fast yellow dye on wool and on cotton with a chromium mordant.

Isatin yellow is a hydrazone prepared by heating a mixture of phenylhydrazine sulphonic acid and **isatin** (*q.v.*) in water.



Isatin.

The colouring matter is precipitated by neutralisation with sodium carbonate and the addition of salt. It has the formula



It is a yellow powder soluble in water, dyeing animal fibres a greenish-yellow in an acid bath.

Phenanthraquinone red is an osazone made from phenanthraquinone $\begin{matrix} C_6H_4CO^* \\ | \quad | \\ C_6H_4CO \end{matrix}$ and α-naphthylhydrazine (sulphonic acid prepared by the reduction of diazotised α-naphthylamine sulphonic acid) and has the formula

$$\begin{matrix} C_6H_4C = N - NHC_{10}H_6SO_3ONa \\ | \quad | \\ C_6H_4C = N - NHC_{10}H_6SO_3ONa \end{matrix}$$

The method of preparation is similar to that given above for isatin yellow. The last three dyes are similar to auramine in respect of their chromophore.

Phenanthraquinone red is a brownish-red powder, which dissolves in water and dyes wool red in an acid bath.

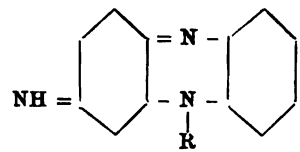
Aniline Black.—When a solution containing aniline is treated with an oxidising agent, the aniline loses hydrogen and becomes converted into aniline black, the structure of which is not understood, though its percentage composition is identical with that of azobenzene, and it may, therefore, be written $(C_6H_5N)_n$; the probable value of n is 3. It is insoluble in nearly all solvents, strong sulphuric acid constituting an exception, so that it can be used with difficulty as a dyestuff; its preparation may, however, be conducted *in situ*, a method which is applied in calico-printing and cotton-dyeing. It is less suitable for wool on account of the attack of the fibre by the necessary oxidant. For effecting the oxidation a variety of agents will serve, but potassium chlorate (or more commonly the sodium salt) is preferred, and it is advantageous to use a metallic salt capable of acting as an oxygen carrier. If chlorate without a carrier be used, aniline chlorate is produced; this is fairly stable in solution, so that the black is only formed when the fabric is dried and the aniline chlorate broken up. For the carrier many compounds capable of readily passing to and fro between two states of oxidation may be used—*e.g.*, those of copper ($CuCl_2$, Cu_2Scy_2, CuS, $CuSO_4$), vanadium (NH_4VO_3), cerium ($Ce_2(SO_4)_3$), as well as potassium ferrocyanide (K_4FeCy_6). Copper salts are most generally used, yielding the most stable blacks. Since soluble copper salts attack the iron and copper of the printing machines, copper sulphide and cuprous thiocyanate are preferable. In cotton printing, a mixture of an aniline salt (100 parts), (generally hydrochloride,† which, how-

* Made by oxidising the portion of crude anthracene (containing phenanthrene) which boils between 310° and 340° C. = 590° and 644° F., with chromic acid in the manner already described for the manufacture of anthraquinone.

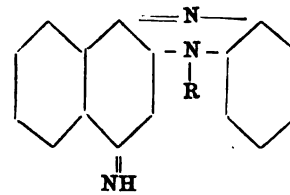
† Excess of hydrochloric acid appears to lead to the tendering of the fabric by the formation of "oxycellulose." Aniline itself may be dissolved in aniline hydrochloride to minimise this difficulty.

ever, may be replaced by a double sulphate of potassium and aniline), sodium chlorate (20 parts), copper sulphate (20 parts),* ammonium chloride (10 parts) and 400 parts of water, together with a thickening agent (starch or dextrin), is applied to the fibre, and the goods are aged by exposure to air at a temperature of 30° C. = 86° F. For dyeing, potassium bichromate is used as an oxidant in sulphuric acid solution, and the thickening is omitted, the aniline black being precipitated in the fibre and not in the bath. The bath is heated, after the goods have been introduced, to a temperature of 75° C. = 167° F. The tendency of aniline black to "green," appears to be connected both with the extent of oxidation and with the composition of the salt used. If the goods have been aged or dyed at too low a temperature, the oxidising action, to a certain extent, stops at the formation of the bodies **emeraldin** and **nigraniline**, substances less oxidised than true aniline black. The highly purified aniline oil (aniline for blue, *q.v.*) now in the market, yields blue-blacks which green easily. The presence of orthotoluidine corrects this tendency, but if excess be present rusty shades are obtained. With wool, it has been proposed to use a somewhat acid bath on account of the greater stability of wool fibre in acid solution.

Indulines.—These substances form a class of dyestuffs, the constitution of which is still under investigation. They are allied to the azine dyestuffs, but their two nitrogen atoms are not linked together. They are quinoneimide derivatives, but differ from the indamines and other quinoneimide dyestuffs in that they contain a nitrogen ring. The following formula for the simplest induline (**benzene induline**) will show the quinoneimide structure:—

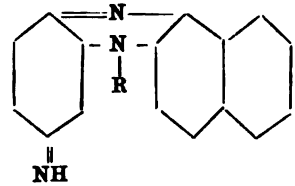


(Here R represents a benzene ring). The other indulines differ from this in respect of the fact that one of the benzene rings (or both) is replaced by a naphthalene ring. Thus, the **rosindulines** are naphthoquinoneimide derivatives of the type

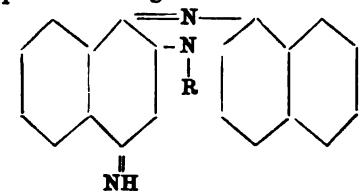


* A much smaller proportion of vanadium salts will serve this purpose (*v.s.*).

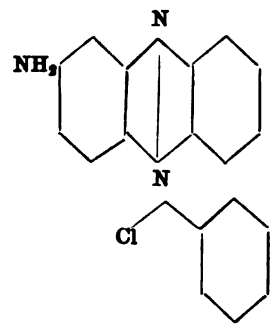
The **isorosindulines** are derivatives of quinoneimide of this form



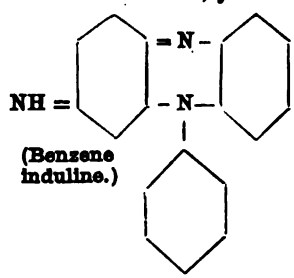
The members of the fourth class of indulines (the **naphthindulines**) contain two naphthalene rings thus—



The connection between that class of azines called the safranines (p. 300) and the indulines, is shown by the preparation of the simplest induline from the simplest safranine. The latter compound—



(**aposafranine**), on the removal of HCl, yields

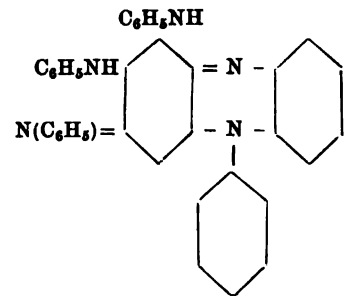


an intramolecular transformation taking place.

The general method of preparing indulines consists in heating amidoazo-compounds with aromatic amines in presence of their salts. Thus, the original method adopted for preparing the dyestuff first known as induline consists in heating a mixture of 100 parts of amidoazobenzene,* 130 parts of aniline hydrochloride, and 300 parts of aniline in a cast iron still, of ample capacity, at 140° to 150° C. = 284° to 302° F. The mass is run into water and made alkaline with caustic soda in order that induline may be precipitated, and unaltered aniline recovered. The induline base obtained in this way is sulphonated, and the sodium salt prepared. The product is known as **induline 3 B.** By heating with more aniline it takes up more phenyl (C_6H_5), and is converted into **induline 6 B.** Besides these indulines, several other benzene indulines are produced by varying the proportion of aniline in the melt, and the temperature at which the reaction is conducted. The nature of the change generally consists in the substitution of phenyl or amidophenyl for hydrogen.

Azodiphenyl blue is the hydrochloride of benzene induline (*v.s.*).

Induline B has the formula $C_{18}H_{15}N_3HCl$.† Induline 3 B is represented by the formula $C_{30}H_{23}N_5HCl$, and induline 6B by $C_{36}H_{27}N_5HCl$—*i.e.*,



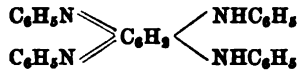
By heating this with paraphenylenediamine, a new dyestuff, improperly called by the already appropriated name toluylene blue (*q.v.*), is obtained.

The substance immediately concerned in the production of

* Amidoazobenzene is prepared by passing nitrous acid into an alcoholic solution of aniline, whereby diazoamidobenzene, $C_6H_5N_2NHC_6H_5$, is formed. This is dissolved in aniline in the presence of a little aniline hydrochloride, and allowed to remain at a temperature of 30° to 40° C. = 86° to 104° F. for a few days. Under these conditions it undergoes intramolecular change becoming converted into amidoazobenzene, $C_6H_5N_2C_6H_4NH_2$.

† The separate existence of this substance is doubtful as its structure is not easily explicable.

induline 6 B is azophenine, which can be isolated from the melt and has the formula

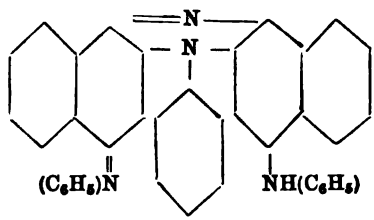


The indulines as a class are bluish-black dyestuffs insoluble in water, mostly soluble in alcohol, although induline 6 B is but little soluble in this menstruum. They are good fast dyes with some affinity for cotton, and are sometimes substituted for indigo. Their sulphonated products are sold as "soluble indulines" on account of their solubility in water. Both indulines and their sulphonated products are used for colouring varnishes and inks.

Another method for preparing dyestuffs of this class consists in heating nitrobenzene with aniline hydrochloride and iron filings. The products are called **nigrosines**. Their constitution and even their empirical formulæ are not known. They are, in comparison with the indulines, somewhat grey in shade, but are otherwise similar.

Rosindulines.—Such dyestuffs of this class as have been prepared, are for the most part not yet of technical importance. By heating nitrosophenylnaphthylamine with aniline, a compound, **phenyl rosinduline**, containing a phenyl group substituted for the H of the NH group in the typical rosinduline quoted above, is obtained. These dyestuffs are similar to the indulines, but have a reddish shade.

Naphthindulines.—**Naphthyl blue** * is a new dyestuff of this class, of the formula (of the type given above),



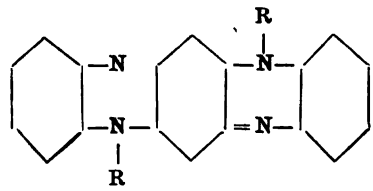
Anilidophenylnaphthinduline.

It is prepared by heating a mixture of benzeneazo-α-naphthylamine hydrochloride, α-naphthylamine hydrochloride and aniline. It dyes silk blue with a red fluorescence.

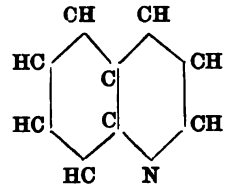
Complex indulines termed **fluorindines** have been prepared by

* This must be distinguished from the older dyestuffs of similar name.

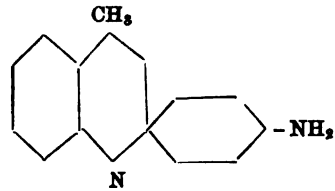
heating azophenines with a dehydrogenating agent. They are of the form



Quinoline Derivatives.—One of these (alizarin blue) has already been mentioned. The constitution of the type-substance, quinoline, may be expressed thus—



the N being substituted for CH of the ordinary naphthalene ring. **Flavaniline** is a dyestuff of this class, being para-amidophenylmethylquinoline



and is prepared by heating acetanilide* with a dehydrating agent—*e.g.*, zinc chloride at a temperature of 250° to 260° C. = 482° to 540° F. The product is extracted with hydrochloric acid, and the dyestuff is salted out. The reaction ultimately consists in the elimination of two molecules of water from two molecules of acetanilide, $CH_3CO{\cdot}NHC_6H_5$; amidoacetophenone, $NH_2{\cdot}C_6H_4{\cdot}CH_3CO$ (the isomeride of acetanilide), is probably an intermediate product.

Flavaniline is not now much used as a dyestuff. It crystallises in colourless needles; the hydrochloride crystallises in yellowish-red prisms, and dyes wool and silk yellow.

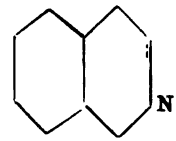
The **cyanines** are basic bodies of the quinoline class, formed by the condensation of two molecules of quinoline, one of which contains a methyl group or one homologous to it (*e.g.*, ethyl or

* Prepared by heating glacial acetic acid with aniline till the mass solidifies on cooling. This product is then distilled.

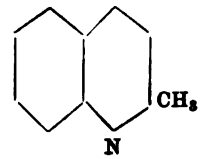
amyl). They are prepared by heating quinoline with methyl quinoline (lepidine),* or a homologue, and methyl iodide or an homologous iodide, and an alkali. HI and H are removed and blue dyestuffs formed.

Iso-amyl cyanine, $C_{29}H_{35}N_2I$, is the best known cyanine. It forms beetle-green crystals, dissolving in alcohol to a blue solution; being fugitive it is but little used as a dye.

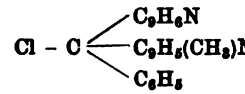
Quinoline red is a derivative of iso-quinoline,



and is prepared by heating iso-quinoline with **quinaldine**,

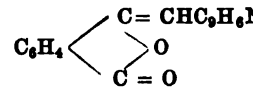


benzotrichloride, $C_6H_5CCl_3$, and zinc chloride. Crude coal tar "quinoline," contains both iso-quinoline and quinaldine, and may therefore be used. The constitution of quinoline red is probably expressed by the formula



It is thus of similar structure to the triphenylmethane dyestuffs. It gives a fluorescent red colour (on silk), but is fugitive to light. It finds application in the preparation of "isochromatic" photographic plates.

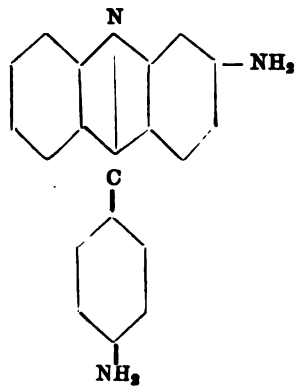
Quinoline yellow or quinophthalone has the constitution



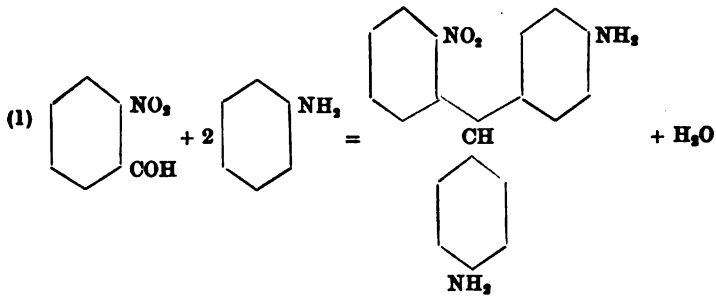
and is produced by heating phthalic anhydride with quinaldine in presence of zinc chloride. Quinoline yellow crystallises in yellow needles. It is not basic. It dyes wool and silk yellow, and its sulphonic acid gives shades like those produced by picric acid. It is fairly fast to light.

* The lepidines are quinolines with the methyl group in the benzene nucleus.

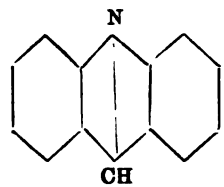
Acridine Dyestuffs.*—Chrysaniline may be taken as a type of these. It is para-amidophenylamidoacridine, having the formula



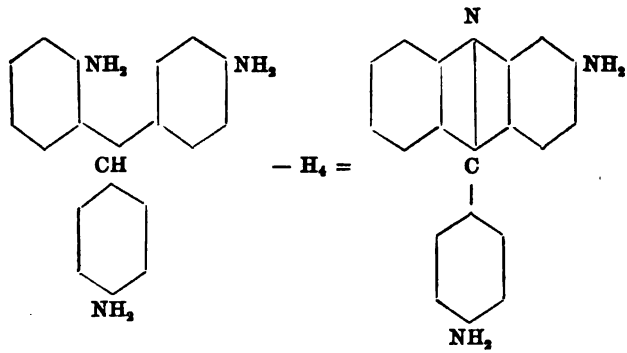
As has been already mentioned, it is a bye-product in the manufacture of magenta (*q.v.*). The commercial product is usually a mixture of the substance shown above and its methyl derivative. The mother liquors from the magenta-melt are precipitated by the addition of salt and lime, the latter throwing down various bases, among which is chrysaniline. The following laboratory synthesis indicates how chrysaniline may be formed in the rosaniline melt from triamidotriphenylmethane, produced by the condensation of one molecule of orthotoluidine with two molecules of aniline. Orthonitrobenzoic aldehyde (corresponding in respect of its substitutions with orthotoluidine) is heated with aniline and zinc chloride, thus—



* Acridine bears a relation to anthracene similar to that borne by quinoline to naphthalene, as is evident from its structural formula,



The reduction of this compound (orthonitroparadiamidotriphenylmethane) converts the nitro-group into an amido-group. When the resulting triamido-compound is oxidised it yields chrysaniline—

(2) 

The precipitate is treated with nitric acid, and the chrysaniline nitrate being sparingly soluble is thus separated, its separation being aided by the addition of a further quantity of nitric acid. The commercial dyestuff (the nitrate, known as **phosphine**) is a yellow powder which dyes silk and wool directly, and cotton with a tannin mordant.

Acridine orange is tetramethyldiamidoacridine,

and is obtained by heating tetramethyltetramidodiphenylmethane with an acid, and oxidising the leuco-compound thus produced.

Benzoflavine is diamidodimethylphenylacridine, and is prepared by condensing benzaldehyde with metatoluylenediamine and heating the resulting tetramidoditolylphenylmethane with hydrochloric acid under pressure. The product is oxidised by means of ferric chloride to benzoflavine. Benzoflavine is a yellow powder slightly soluble in cold water, dyeing wool and silk directly, and cotton with a tannin mordant.

(2) **Natural Organic Dyestuffs.—Indigo.**—This is the product of various species of *Indigofera*, the most important being *I. tinctoria*, chiefly cultivated in the East Indies. Several other species are grown elsewhere, the chief of which is *I. argentea*, the culture of which is practised in Africa (notably in Egypt). Another class of plant, *woad*, *Isatis tinctoria*, yields indigo in small quantity, and is no longer used as a source of the dyestuff. It is grown in Europe, however, to prepare the "woad-vat" for indigo dyeing (*v.i.*). Indigo does not exist as such in these plants, but in the form of a "glucoside," **indican**, $C_{26}H_{31}NO_{17}$, a substance which readily undergoes hydrolysis with the formation of **indigotin**, the colouring matter of indigo, and **indiglucin**, which

has been termed a glucose, although its formula does not correspond with that of the glucoses—

$$\underset{\text{Indican.}}{2C_{26}H_{31}NO_{17}} + 4H_2O = \underset{\text{Indigotin.}}{C_{16}H_{10}N_2O_2} + \underset{\text{Indiglucin.}}{6C_6H_{10}O_6}$$

The preparation of crude indigo from the plant consists in macerating the plant with water, whereby fermentation is set up and hydrolysis of the indican takes place. The indigotin produced by the hydrolysis, however, is reduced during the fermentation process by the indiglucin to **hydrindigotin** (indigo white), $C_{16}H_{12}N_2O_2$, which dissolves in the aqueous liquor, alkaline from the products of fermentation. The liquor is run off the macerated plants into a second vat, and by exposure to air, aided by agitation, the hydrindigotin is reoxidised, and indigotin precipitated—being insoluble in the alkaline liquid. The yield is about 0·2 per cent. of the weight of the plant. The addition of ammonia to the vat is frequently practised, with the result that the yield is largely increased, as the formation of ammonia by the fermentative breaking down of the indigo is thus hindered. When the indigo-blue has settled, the bulk of the liquor is run off, and the blue transferred to a cauldron where it is boiled with water to stop fermentation and to extract soluble impurities. It is then filtered, and the residue pressed into cakes and cut into cubes. The indigo obtained in this manner varies greatly in quality. Its content of indigotin ranges from 20 to 90 per cent., the average being 40 to 50 per cent. The remainder consists of ash, 5 to 20 per cent.; water, 2 to 8 per cent.; **indirubin**, 2 to 4 per cent., and various amounts of **indigo brown**, **indigo-gluten**, and carbohydrates. The value of the blue depends on its content of indigotin and indirubin. **Indigotin** is a dark blue crystalline substance with a bronze lustre; its specific gravity is 1·35; it sublimes and partially decomposes at 290° C. = 554° F. It is remarkable for its insolubility, being unaffected by dilute acids and alkalies, and almost completely insoluble in ordinary organic solvents. Chloroform, glacial acetic acid and aniline dissolve it sparingly. It dissolves in strong sulphuric acid, and is reprecipitated on dilution; if the solution be heated sulphonic acids are formed (*v.i.*). It is soluble in an alkaline liquid in the presence of reducing agents, such as glucose, ferrous hydroxide, stannous oxide, &c. By oxidising agents it is converted into **isatin**

$$C_8H_5NO_2\left(i.e., C_6H_4\begin{<}{CO}{N}\end{>}C(OH)\right)$$

Special attempts have been made to synthesise indigo and to make it as much an artificial colouring matter as is alizarin (*q.v.*), and thus to displace the indigo plant, just as madder has been driven out of cultivation. Hitherto, but little commercial

success has attended these efforts. The most hopeful method of synthesis is that recently devised by Heumann. By heating monochloracetic acid with aniline, phenylglycocine (phenylamidoacetic acid) is formed, thus—

$$C_6H_5NH_2 + CH_2Cl{\cdot}COOH = \underset{\text{Phenylamidoacetic acid.}}{C_6H_5NH{\cdot}CH_2{\cdot}COOH} + HCl$$

One part of this product is heated with two parts of caustic soda at 260° C. = 500° F. in a closed retort, the melt is dissolved in water, and the solution oxidised by a current of air. The reaction may be represented as taking place in two stages—

(1) $C_6H_5NH{\cdot}CH_2{\cdot}COOH = C_6H_4\begin{cases}CO\\NH\end{cases}CH_2 + H_2O$

Pseudo-indoxyl.

(2) $2\left(C_6H_4\begin{cases}CO\\NH\end{cases}CH_2\right) + O_2$

$$= C_6H_4\begin{cases}CO\\NH\end{cases}C{=}C\begin{cases}CO\\NH\end{cases}C_6H_4 + 2H_2O$$

Indigotin.

Another process of interest, though at present of little commercial importance, consists of the following steps :—

Orthonitrobenzaldehyde, prepared from orthonitrobenzyl chloride (by a process not made public), is heated with acetone and an alkali, the following reaction taking place :—

$$C_6H_4(NO_2)CHO + (CH_3)_2CO = C_6H_4\begin{cases}CH(OH)CH_2CO(CH_3)\\NO_2\end{cases}$$

Nitrophenyllactomethyl ketone.

By further treatment with alkali, this is converted into indigotin and alkali acetate. It has not been found advisable to prepare indigotin in this way and to separate the product; by converting the ketone into its sodium bisulphite compound, however, a soluble substance is obtained which can be printed on a fabric and transformed into indigotin *in situ* by treatment with an alkali. Obviously, goods can be dyed by soaking them in a solution of the ketone compound, and passing them through a bath of caustic alkali.

Two or more isomerides of indigotin exist. The most important of these is indirubin the relation of which with indigotin may be shown by the formula

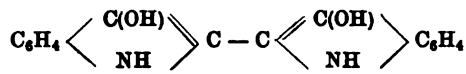
$$C_6H_4\begin{cases}CO\\NH\end{cases}C:C\begin{cases}CO\\C_6H_4\end{cases}NH$$

It is a red crystalline substance, constantly present in commercial

indigo, and accompanying it throughout the dyeing process (*q.v.*).

The chromophoric group in these compounds is

As there is no salt-forming group in indigotin, this substance, as has been pointed out at the beginning of the section, owes its fastness as a dye to its insolubility and not to chemical attachment to the fibre. This is evident from the fact that it rubs off to a slight extent, although otherwise an extremely permanent colour. All the colouring matters in commercial indigo are capable of conversion, by reduction, into colourless derivatives, soluble in alkalies. Such derivatives of colouring matters are known by the generic prefix "leuco" (white). They generally contain more hydrogen than is present in the colouring matter. Thus, **indigo-white** (**leucindigo**, reduced indigo, hydrindigotin) has the formula



The application of indigo as a dye depends upon this formation of indigo-white. The principle underlying all processes of indigo "vat" dyeing (as distinct from dyeing with indigo-sulphonic acids—*v.i.*), is the reduction of indigo to indigo-white and the dissolution of the resulting indigo-white, in an alkali; the fibre to be dyed is saturated with this solution, and exposed to the air, whereby the indigo-white is rapidly oxidised and indigo-blue formed in the interstices of the fibre. In practice, many kinds of vat can be used. It will suffice to describe three as types, viz.:—The copperas (ferrous sulphate) vat (used for cotton), in which ferrous hydroxide is the reducing agent; the woad vat (used for wool) in which the reducing action of a ferment is employed; and the hyposulphite vat used for both wool and cotton. An average copperas vat will contain 30 lbs. of finely-ground indigo, 80 lbs. of ferrous sulphate, 60 to 100 lbs. of slaked lime, and 1,000 gallons of water. The slaked lime reacts with the ferrous sulphate, producing ferrous hydroxide and calcium sulphate. The former, in presence of excess of lime, reduces the indigo to indigo-white, which dissolves in the alkaline bath. Several vats are worked in series systematically, the cloth passing from the weaker to the stronger vats. The excess of liquor is squeezed out when the cloth leaves the last vat, and the indigo-white is oxidised to indigo by exposure to air, during passage of the cloth over rollers. This vat is not suitable for dyeing wool, on account of the large quantity of lime which it contains, wool being more susceptible of injury by the attack of alkali than is cotton. The woad vat can be worked with a small quantity of lime, and is therefore to be preferred for wool

dyeing. The woad is used in the form of balls of dried leaves of the woad plant (*Isatis tinctoria*) which, although containing but little indigo, is said to be valuable in imparting a good shade to the dyed material. Its main use, however, is to excite fermentation in the indigo vat. For the same purpose bran and madder are used. The vat is generally composed of indigo 10 to 25 lbs., woad 1½ to 5 cwts., bran 20 lbs., madder 5 to 20 lbs., slaked lime 24 lbs., water 1,500 gallons. The woad is first added to the water, which is heated to 60° C. = 140° F.; after some hours the finely-divided indigo, madder and bran are added, together with half the lime. Fermentation sets in, and when a piece of wool dipped into the vat is found to become blue on exposure to air, the rest of the lime is gradually added, the temperature being maintained at 60° C. = 140° F. The organism chiefly concerned in the fermentation is a pathogenic bacillus, resembling that characteristic of pneumonia. Recently, an improved vat, said to avoid loss of indigo, has been prepared by adding a cultivation of the organism *Desmobacterium hydrogeniferum*, and substituting flour and glucose (as nutrient materials) for the bran, &c., and soda and magnesia for the lime. The general method of dyeing is similar to that described above.

The hyposulphite* vat, applicable both to wool and cotton, is prepared as follows:—Zinc sheet is allowed to act on a strong solution of sodium bisulphite, producing zinc hyposulphite (ZnS_2O_4). The operation is conducted in a closed vessel, as the hyposulphites are readily oxidised by air. The solution is mixed with milk of lime and indigo (20 lbs. of indigo, 25 lbs. of slaked lime and 20 gallons of water), and heated to about 70° C. = 158° F., whereby indigo is reduced and dissolved. The strong solution of reduced indigo is added, as required, to a vat containing 60 to 70 lbs. of sodium sulphite, 6 lbs. of zinc dust and 6 lbs. of lime (to complete the reduction of the indigo). The process of dyeing is essentially the same as has been already described. The hyposulphite has a somewhat drastic action on wool, so that the use of this vat with that material requires care.

The **indigo-sulphonic acids** are used in dyeing wool and silk under the name of "indigo-extract" and "Saxony blue," but cotton cannot be dyed by these substances. These dyestuffs are not ingrain colours, as is indigo, but dye by direct absorption into the fibre; cotton fibre, being incapable of exercising this attraction, cannot be dyed with them. The shades produced are not fast to washing. The indigo-extract is generally made in the dye house by stirring finely-powdered indigo with about 6 times its weight of concentrated sulphuric acid and heating to about 60° C. = 140° F. The solution is diluted with water and

* Not to be confounded with thiosulphate, commonly called "hyposulphite."

the dyestuff is salted out by the addition of sodium chloride, an acid sodium salt of indigo-sulphonic acid being formed. By repeating the treatment, the neutral sodium salt is obtained. According to the proportion of sulphuric acid used, its strength and the temperature of treatment, indigo-monosulphonic acid, $C_{16}H_9N_2O_2(SO_2OH)$, or indigo-disulphonic acid, $C_{16}H_8N_2O_2(SO_2OH)_2$, or a mixture of the two is formed. When the disulphonic acid is specially required, fuming sulphuric acid is used for dissolving the indigo. The monosulphonic acid has a reddish shade and is known as **purple indigo-extract**, while the disulphonic acid is blue; its sodium salt is called **indigo-carmine**. The monosulphonic acid is soluble in pure water, but insoluble in dilute sulphuric acid. The disulphonic acid is a blue powder soluble in water and dilute acid. Both acids are precipitated by the addition of salt or sodium sulphate.

With regard to printing with indigo, it was formerly only possible to produce a pattern by printing a discharge (*v.i.*) upon the dyed fabric. According to modern practice, a system is adopted equivalent to the formation of a true indigo vat in the fibre itself. This is done by saturating the fabric with a solution of glucose, and printing finely-divided indigo, mixed with strong caustic soda. By steaming, the action between the indigo and the glucose in the printed pattern is accelerated, and the reduced indigo, which results, penetrates the fibre wherever printed. On exposure to air, the indigo white is oxidised and the pattern becomes dyed blue.

Logwood is the heart-wood of *Hæmatoxylon campechianum*, a tree growing in Central America. When freshly cut the wood is nearly colourless, but it soon reddens externally on exposure to air. The colouring matter is an oxidation product of the body **hæmatoxylin**, $C_{16}H_{14}O_6$, the constitution of which is unknown.

This oxidation product is **hæmatein**, $C_{16}H_{12}O_6$, which has a bronze green colour in the mass, but yields a red solution; it is also of unknown constitution. In order to convert the whole of the hæmatoxylin of the wood into hæmatein, the chipped or rasped wood is exposed in heaps, until fermentation sets in (known as the "ageing" of the wood, and supposed by some to consist in the decomposition of a glucoside, yielding hæmatoxylin). A small quantity of ammonia is formed during fermentation, and aids the oxidation, hæmatoxylin being readily changed into hæmatein in the presence of an alkali. The wood is either used in chips to make up the dye-bath, or its aqueous extract is employed. This is prepared by systematic extraction with hot water and concentration of the solution thus obtained, in a vacuum pan. Although itself a red colouring matter, logwood is used for producing other colours, notably blues and blacks. It is not a dye but a dyestuff, and as textile fibres have no affinity for it,

it must always be used with a mordant, the nature of which modifies the colour produced. Thus, chromium mordants give blue passing to black; iron, grey passing to black; aluminium, dull-violet; copper, greenish-blue; tin, reddish-violet. A mixture of mordants may be used and mixed shades produced. The colours are fairly fast, though the blue is not so fast as that produced by indigo. Logwood is used for dyeing cotton, wool and silk, especially for producing black dyes. An **iso-hæmatein** has been prepared from ordinary hæmatein and is said to be faster than its isomeride, but it is not yet of technical importance.

Brazil Wood.—This wood, together with a number of other woods—*e.g.*, peach wood, sapan wood and Lima wood, all belonging to the leguminous genus, *Cæsalpinia*—contains **brazilin**, $C_{16}H_{14}O_5$,* a colourless substance of unknown constitution, but apparently similar to hæmatoxylin. This substance is present in the wood as a glucoside, and for the purpose of hydrolysing this, the wood is submitted to a process of fermentation analogous to that adopted for logwood. At the same time the brazilin suffers oxidation to **brazilëin**, $C_{16}H_{12}O_5$,† the change being hastened by the presence of an alkali, as in the case of logwood. The shades produced by brazilëin are fugitive to light, and are not fast to soap. The colours obtained by means of brazil wood depend on the mordant—*e.g.*, chromium mordants yield a violet or claret; aluminium, rose-red; iron, dull violet or purple; copper, drab or brown; tin, crimson.

The above woods have an open texture, and are termed "soft or open woods." They readily yield their colouring matters on extraction. Another group of woods of the same class—*e.g.*, santal wood, cam wood and bar wood—are known as "close woods," and are less easy to extract. They yield colouring matters similar to brazilëin, and are similar in other respects to the woods already described.

Old fustic or **Brazilian yellow wood** is the wood of *Morus tinctoria*, obtained from Brazil and the West Indies. Its colouring matter is **morin**, $C_{13}H_8O_6 \cdot 2H_2O$, the constitution of which is not known. Fustic is applied like the woods already mentioned, either as chips or extract, and gives bright yellow shades with tin and aluminium mordants. It is also used as an adjunct to logwood, improving the blacks obtained by means of this dyestuff.

Young fustic or **fustet wood** is the wood of *Rhus cotinus*, and contains the glucoside **fustin**, which yields the colouring matter **fisetin**, $C_{23}H_{10}O_8(OH)_6$, and a sugar on hydrolysis. The wood is used as chips, or an extract (termed **cotinin**) is obtained from it. It is a yellow dyestuff, but is mainly employed together with other dyestuffs—*e.g.*, cochineal—for wool dyeing.

* Another formula, $C_{22}H_{16}O_7$, has been proposed.

† Another formula, corresponding with that for brazilin, is $C_{22}H_{16}O_7$.

Quercitron bark is the inner layer of bark from *Quercus tinctoria*. The main part of the colouring matter is contained in the yellow powder which is obtained, mixed with woody fibre, when the bark is ground. The glucoside **quercitrin**, $C_{36}H_{38}O_{20}$, is the source of the yellow colouring matter **quercitin**, $C_{24}H_{16}O_{11}$, which it yields on hydrolysis, together with a pentose, rhamnose, $C_6H_9(CH_3)O_5 \cdot H_2O$. Both quercitrin and quercitin are dyestuffs yielding yellow shades with aluminium mordants, and orange shades with tin mordants. The product obtained by acting on the bark with dilute sulphuric acid, commercially known as "flavin," contains both quercitrin and quercitin. It is sold as a concentrated form of quercitron. It is used with cochineal in scarlet dyeing.

Weld, the leaves of *Reseda luteola*, contains luteolin, $C_{20}H_{14}O_6$,* which gives fast yellow colours with aluminium mordants and is used for silk dyeing.

Turmeric is the colouring matter obtained from the rhizomes of *Curcuma tinctoria*. The colouring principle **curcumin**, $C_{14}H_{14}O_4$, is capable of dyeing cotton without a mordant; it is used for modifying red shades thereon. It is not fast to light. Besides its use as a dyestuff it is employed as an indicator.

Persian berries are the fruit of *Rhamnus amygdalinus*. They contain the glucoside **xanthorhamnin**. Hydrolysis converts this into rhamnotin and isodulcitol (rhamnose), thus—

$$C_{48}H_{56}O_{29} + 5H_2O = \underset{\text{Rhamnotin.}}{2C_{12}H_{10}O_5} + 4C_6H_{14}O_6.$$

When dyed with tin, or tin and aluminium mordants, it gives a fine yellow colour. It is used chiefly as an extract.

Safflower is the flower of *Carthamus tinctorius*, and contains the colouring matter **carthamin**, the formula for which is doubtful. It is found in commerce as an extract, which is dissolved in soda to form the dye-bath, and then acidified with citric acid. It produces a pink colour on silk. It is mixed with starch to make toilet rouge.

Catechu or **cutch** is obtained as an extract from various species of acacia. (Gambier is a similar material.) It contains **catechin** ($C_{21}H_{20}O_9 5H_2O$) which is itself colourless, but gives a fast brown on cotton when oxidised, after passage through the dye-bath, by potassium bichromate.

Lichen Colouring Matters.—The following are the kinds of lichens which are commercially important from the colouring matters which they yield—*Roccella tinctoria*, *R. fuciformia* and *Lecanora tartarea*. These are commercially known as orchella or orchil weed. The lichens contain **orcinol** or **orcin**, a dihydroxytoluene. This body occurs to a slight extent in the free state, but for the most part results from the decomposition of **orcellic**

* Some authorities give $C_{12}H_8O_5$.

acid polymeric with **orcellinic** acid; the latter is **dihydroxytoluic** acid of the formula $C_6H_2CH_3(OH)_2COOH$. **Erythrin**, $C_{20}H_{22}O_{10}$, is another compound which yields orcinol on decomposition. **Archil** is prepared preferably from *Roccella tinctoria* by moistening the shredded weeds with ammonia, and keeping the mass at a temperature of about 40° C. = 104° F. for some days. During this process various decompositions occur, one of the products of which is orcinol; this becomes **orcein** by oxidation in presence of the ammonia. The orcein contains nitrogen, and has the formula $C_{28}H_{24}N_2O_7$ allotted to it by some authorities. The commercial product is sold either as a liquor or paste.

Cudbear (*perseo*) is similarly prepared, *Lecanora tartarea* being preferred as the raw material. It is a dark brown or purple powder.

For preparing **litmus** a longer treatment of the lichens and the addition of potassium carbonate are necessary. The concentrated extract is mixed with plaster of Paris and cut into cubes. Litmus is not used as a dyestuff, but for colouring wine and as an indicator in the laboratory.

The above three dyestuffs are used largely in conjunction with other colouring matters, notably indigo. Archil and cudbear are dyed on wool and silk from acid baths, yielding bluish-red shades.

Cochineal.—This is one of the few dyes of animal origin. The commercial material consists of the bodies of females of the insect *Coccus cacti*, collected from certain kinds of cactus in Mexico and the Canary Islands. Three grades are known, "silver grain" (the best), "black grain" and the inferior "granilla." These are said by some to be insects in different stages of maturity, but by others it is stated that their difference largely depends on the mode of collection and drying—the black having been killed by boiling water, and the silver stove-dried. The white film on the silver grain cochineal is due to the wax **coccerin**, $C_{30}H_{60}(C_{31}H_{61}O_2)_2$ (cocceryl coccerate), naturally present, and amounting to about 1 to 2 per cent. of the weight of the cochineal. This silvery coating is often imitated by facing the cochineal with talc and other mineral matter. Cochineal contains about 10 per cent. of the red colouring matter "**carminic acid**," which is a glucoside and splits up on hydrolysis, yielding the true colouring matter **carmin**, and a sugar, thus—

$$\underset{\text{Carminic acid.}}{C_{17}H_{18}O_{10}} + 3H_2O = \underset{\text{Carmin.}}{C_{11}H_{12}O_7} + C_6H_{12}O_6.$$

The dyeing process consists in immersing the goods (generally wool) in a decoction of cochineal containing the appropriate mordant, tin for scarlet, chromium for purple, aluminium for crimson. Bluer shades are obtained by the use of ammoniacal cochineal,

prepared by moistening ground cochineal with ammonia, leaving the mass for some days, adding precipitated alumina and heating until the ammonia is expelled. The product of the action of the ammonia appears to have the formula $C_{17}H_{17}(NH_2)O_9$. The alumina-lime lake of carminic acid is used as a pigment under the name "carmine"; it must not be confounded with carmin, the product of the hydrolysis of carminic acid.

Kermes is the insect *Coccus ilicis*, collected from the *Quercus ilex*, the habitat of which is Spain and North Africa. Its colouring matter is closely allied to that of cochineal, and it served at one time similar purposes as a dyestuff.

Lac-dye.—This is a colouring matter which is dissolved from stick lac (see *Shellac*) on treatment with water. The colouring matter is precipitated from the solution by addition of an aluminium salt, and the lake is pressed into cakes. When used as a dyestuff it produces a colour similar to, but faster than, cochineal; it is, however, less brilliant. It is stated that the colouring principle is not identical with that of cochineal, but is laccainic acid, $C_{16}H_{12}O_8$.

(3) **Mineral Dyes.**—But few mineral colouring matters are capable of being advantageously used either as dyestuffs or dyes. Those which are in use are ingrain dyes, comparable with indigo (*q.v.*) precipitated in the fibre.

Chrome yellow (lead chromate, $PbCrO_4$) is applied to cotton, for which alone it is used, by passing the fabric first through a solution of lead nitrate or acetate, precipitating the lead as hydroxide in the fibre by means of an alkaline bath, or as sulphate by means of a bath of sodium sulphate, and converting this into lead chromate by passing through a bath of sodium bichromate.

Chrome orange (basic lead chromate) is prepared in the fibre by first impregnating it with chrome yellow as described above, and then immersing it in a bath of boiling lime water.

Manganese Brown, "Bistre."—Fabrics may be dyed with manganese peroxide by saturation with manganous chloride and precipitation of manganous hydroxide in the fibre by passage through an alkaline bath. Passage through a solution of chloride of lime converts the manganous hydroxide into the brown hydrated peroxide.

Another reddish-brown is obtained from manganese and iron salts, which is more resistant to acids than true iron brown (iron buff—*q.v.*).

Iron Buff—Nankin Yellow.—This is produced in two shades, by passing the fabric (cotton) through a solution of ferrous sulphate and then through one of caustic soda. The ferrous hydroxide is either oxidised by exposure to air or by treatment with chloride of lime. Ferric salts may also be directly used.

Prussian blue was formerly of some importance, but has been largely displaced by synthetic organic dyestuffs. There are two

methods for producing Prussian blue in the fibre. The one consists in producing ferric hydroxide in the fibre (*v.s.*) and converting this into Prussian blue by immersion in an acid solution of potassium ferrocyanide. The other consists in saturating the fabric with an acid solution of a ferro- or ferricyanide, and raising the temperature to boiling point, whereby the hydroferrocyanic or hydroferricyanic acid first liberated, is decomposed with the formation of a blue pigment.

B. **DYEING AND MORDANTS.**—The methods of bringing the material to be dyed into contact with the dyestuff naturally vary according to the nature of the material, and the use to which it is to be put. Thus, if the fabric is to be of one uniform colour it suffices to dye it "in the piece"—*i.e.*, after it has been woven. Where a coloured pattern has to be produced (other than by printing methods) threads of different colour have to be employed in the weaving, and the material is dyed as yarn. In some instances stuff that is ready to be spun into yarn is dyed previously to its being further worked up. The details of the apparatus for bringing the material into contact with a dyestuff are purely matters of mechanical engineering and cannot be considered in detail here. It suffices to say that their main object is to bring the dyeing liquor into rapid and perfect contact with the stuff to be dyed. The processes most used fall into two main groups. In the first the stuff is stationary and the dye liquor is caused to filter through it; in the second the liquor is stationary and the stuff is made to travel through it, often as an endless band. The various mechanical terms, such as "hank-dyeing," "cop-dyeing," &c., have reference to the form in which the material is made up before being put through the dye-bath, such preliminary fabrication being in many cases an early stage in the process of manufacture.

With regard to the constitution of the dye-bath, this depends primarily upon that of the fibre to be dyed. Thus, in general terms, the marked chemical activity of silk and wool permits their being dyed directly (although mordants are often used as auxiliaries), whereas the comparative inertness of cotton and similar cellulosic materials necessitates the use of a mordant, in all but a few cases of dyestuffs which are chiefly of quite recent invention. In the foregoing description of dyestuffs, the structure and mode of formation have served as a means of classification. In the ensuing consideration of the application of these dyestuffs, a broad division into (1) acid dyestuffs, (2) basic, (3) indifferent, will be found more convenient, for it is upon the properties thus connoted that the selection of an appropriate mordant for a given dyestuff depends. In general, an acid dyestuff will require a basic mordant, and thus a classification complementary to that given above will be valid for mordants. Seeing that the application of dyestuffs is also in-

fluenced by the nature of the fibre to be dyed, the following classification based on a consideration of both the dyestuff and the fibre will be found convenient:—

1. Direct Dyes, applicable to all fibres.
2. Basic Dyes, also applicable to all fibres.
3. Acid Dyes, applicable to wool and silk.
4. Mordant Dyes, applicable to all fibres.
5. Special Dyes, requiring special processes.

The subject of mordants may be dealt with before that of the processes of dyeing.

Mordants.—These are a group of bodies which are used in dyeing and printing textile fabrics with the second and fourth of the groups of dyes named above, for the purpose of fixing the colour more firmly on the fabric; in some cases the mordant aids in the development of the colour as well as in its fixation.

(1) **Basic Mordants.**—The object of these mordants is to impregnate the fabric with a basic oxide capable of uniting with the dyestuff used which has acid properties, to form a chemical compound commonly known as a "colour lake." The constitution of these "colour lakes" will be dealt with later.

The salts used to supply the basic oxide, which is to serve as a mordant, are generally those of aluminium, iron, chromium and tin. Of these, the iron mordants have a "saddening" effect—*i.e.*, give somewhat dark shades (a property possessed also by copper salts).

Aluminium Mordants.—The principal salts used are alum and aluminium sulphate. Since aluminium sulphate is a moderately stable salt, it is necessary to convert it into a salt more easily broken up by the influence of the affinity of the fibre. For this purpose, an organic acid, generally tartaric acid in the form of bitartrate of potash (cream of tartar), is used. It is generally supposed, as a working hypothesis, that aluminium tartrate is formed, which is broken up by the action of the fibre and the liberated alumina absorbed by the fibre. This is more particularly applicable for wool, the fibre of which has a slight but definite acid character. In the case of silk, it is necessary to use an actual precipitant for the alumina in the form of calcareous water. Another modification often employed for cotton consists in impregnating the material to be dyed with a solution of aluminium acetate, and "ageing" it, either by exposure in a warm atmosphere whereby a portion of the acetic acid is driven off, or by steaming in a closed vessel.

The aluminium acetate may also be decomposed by passage of the fabric through a weak alkaline bath—*e.g.*, of sodium phosphate or arsenate. Aluminium thiocyanate is sometimes used, being, like the acetate, capable of easy decomposition. The cotton fabric may also be first impregnated with tannic

acid or "Turkey-red" oil (*q.v.*) and subsequently with aluminium sulphate. Sodium aluminate is another form in which aluminium may be applied to cotton, its alumina being deposited by the decomposition of the salt by the carbonic acid of the air.

Iron Mordants.—These are mainly ferrous sulphate and acetate, the corresponding ferric salts and the so-called "nitrate of iron"—crude ferric sulphate. The general methods are similar to those for aluminium mordants. In addition, when ferrous salts are used, ageing and consequent oxidation are carried out, the ferric salt produced acting better as a mordant than does a ferric salt directly applied to the fibre. Passage through weak alkaline baths is practised, especially for "nitrate of iron," much used in dyeing cotton.

Chromium Mordants.—The salts of chromium (from the oxide, Cr_2O_3) are analogous in their behaviour to those of aluminium. Chromic sulphate can be used for mordanting wool, and the more easily decomposable acetate and thiocyanate for cotton. Another form of chromium mordant for wool is the fluoride, CrF_3, which is useful on account of the ease with which it is decomposed, and the absence of injurious action of the hydrofluoric acid—liberated by its decomposition—on the fibre and dyestuff. An alkaline solution of chromic hydroxide is also used as a mordant. Weak alkaline baths, to follow those of neutral chromium salts, are used in the case of cotton, the rationale of the proceeding being the same as with aluminium. Sodium or potassium bichromate may also be applied as a mordant. The fibre apparently fixes chromic acid from this, the chromic acid being subsequently reduced to chromic hydroxide by passage through a bath containing an organic acid or a bisulphite, or in the dye-bath itself at the expense of the dyestuff, fibre or some other constituent. Chromic acid thus used and reduced by an organic acid (*e.g.*, oxalic acid) or an organic salt (*e.g.*, tartar, bitartrate of potash) constitutes what is termed a "non-oxidising mordant"; should no such reducing agent be employed *ad hoc*, the phrase "oxidising mordant" is appropriate; when chromic acid is utilised in this manner the dye must be such a one as logwood, upon which an oxidising action is required.

Tin Mordants.—Tin is used in the form of both stannous and stannic compounds. Stannous chloride (tin crystals) is used as a fixing agent for tannin mordants in cotton dyeing, and in the dyeing of Turkey reds and wood colours on cotton, and in dyeing wool and silk. Stannic chloride is used in silk dyeing. Stannate of soda is largely used in calico-printing for preparing the cloth for printing many dyes, such as the eosins. The cloth is first passed through a solution of the stannate, and then through a weak bath of sulphuric acid, whereby a deposit of stannic oxide is formed on the fabric.

(2) **Acid mordants** are employed for fixing basic dyestuffs on

such materials as do not fix them directly. Wool fixes basic dyestuffs directly (in the absence of any notable addition of acid) and, therefore, needs no external mordant. A small quantity of acetic acid may be added, however, to the dye-bath, if the water be calcareous or the wool alkaline from the washing it has undergone. Soap is sometimes used as an aid to dyeing wool, its function probably consisting in providing a fatty acid capable of union with the basic dyestuff. Silk is also dyed from a feebly acid bath, or the bath may be neutral or alkaline with soap, or "boiled-off liquor"—*i.e.*, the solution of the sericin of silk fibre in soap (see *Textiles*, Vol. II.). The colours on silk are sometimes made more brilliant by subsequent passage through a feebly acid bath. All these processes are in the highest degree empirical. For cotton, on the other hand, definite acid mordants are required. The mordant may be tannin, or fatty acids or an acid dyestuff. The tannic acid generally requires to be fixed on the cotton in the form of the salt of some feeble base (*e.g.*, antimony or tin oxide), so that a bath of tartar emetic or stannic chloride (or pink salt—*q.v.*) usually follows that of tannic acid. The acid combined with the basic colour is displaced by the tannic acid held on the fibre, and the dyestuff thus enters into combination with the "tanned" fibre to form a dye upon it. Various forms of tannin (*q.v.*)—*e.g.*, gall-tannin and sumach—are used in this manner, the purified tannic acid from gall-nuts being preferred for delicate colours. The effect of the tannin is referable to the fact that in the presence of sodium acetate all basic colouring matters may be precipitated by tannin solution, a reaction which distinguishes them from dyestuffs of acid character. The commonest form in which antimony oxide is used is tartar emetic,

$$C_2H_2(OH)_2 \begin{matrix} COO(SbO) \\ COOK \end{matrix}$$

but more recent preparations, avoiding the expense of the tartaric acid, are the double oxalate of antimony and potassium, $SbK_3(C_2O_4)_3$, the double fluoride SbF_3NaF and the salt $SbF_3(NH_4)_2SO_4$. The essentials for an antimony salt for this purpose are that it shall be soluble in water without precipitation of antimony oxide, and yet be readily decomposable to act as a mordant. Of other acid mordants it may be said that fatty acids are generally applied by saturating the fibre with a solution of soap, drying and steeping in a solution of aluminium sulphate, the aluminium salts of fatty acids thus formed in the fibre serving as a mordant for the basic dyestuff. The application of Turkey-red oil has already been described (p. 282). When acid dyestuffs are used as mordants it is generally for the purpose of producing a compound shade. Alizarin, logwood and aniline black frequently serve as bottoms in this way for basic dyestuffs.

The application of the foregoing principles may be illustrated by the following description of various methods of dyeing.

Cotton Dyeing.—(A) **With Direct Dyestuffs.**—The dyeing of cotton with the direct or substantive dyes, of which Congo red (p. 277) and other dyestuffs of the benzidine class, such as benzopurpurin, chrysophenin, diamine red, Titan red, azo-blue and toluylene orange, are examples, is a comparatively simple matter. A dye-bath is prepared containing the dyestuff or dyestuffs together with a quantity of common salt—10 per cent. to 20 per cent.—sodium sulphate (Glauber's salt), soap, soda or a mixture of these according to the nature of the dyestuff; the cotton is treated in this bath at the boil for about an hour. A satisfactory explanation of the cause of the affinity of these direct colouring matters for cotton has not been formulated; the precise function of the various salts which are added to the dye-bath is still unknown; it is probable that they modify the solubility and the state of aggregation of the colouring matter; it is known, however, that a certain minimum quantity is required for each dye to obtain the best results, while, on the other hand, an excess throws the dye out of the bath and poor results are obtained. Of the many direct dyes which are now available, some are fast to alkalies and others to acids; the yellows are distinguished by their fastness to light, but the majority of the other colours are fugitive. Certain of these dyes—*e.g.*, benzoazurin 3 G, benzochrome black, diamine blue—are used, not only as substantive dyes, but also with a copper or zinc mordant, by first dyeing the cotton in the usual way and then treating it in a solution of a zinc or copper salt, which fixes the dye on the fibre. Often this treatment is accompanied by some change of tone of the colour on the fibre. Some of the direct dyestuffs, primuline, diamine blacks, diazo-blacks, Zambesi blues, &c., contain amido-groups in their composition which are capable of undergoing diazotisation; the products can be combined with other bodies—*e.g.*, phenols and amines—to form new dyes termed "ingrain colours," which are fast to washing and other bleaching agencies. The method of thus "developing" a colour on the fabric is capable of many modifications, and its use is growing. The process takes place in three stages—1st, the cotton is dyed with the dyestuff in the usual manner; 2nd, it is passed into a cold bath of sodium nitrite, acidified with hydrochloric acid, for the purpose of "diazotising" it; and 3rd, it is introduced into a bath of some "developer" to complete the production of the ingrain colour. The developers chiefly used are phenol, beta- and alpha-naphthol, resorcinol, alpha- and beta-naphthylamine, phenylene diamine, toluylene diamine, and sulpho-acids of these bodies. The phenols and naphthols are used in alkaline solution, and the amines in acid solutions. A great variety of shades can be obtained.

(B) **With Basic Colours.**—The basic colours require the cotton to be mordanted with tannic acid (see *Mordants* above); dyeing with this class of colouring matters takes place in three stages—(1) The cotton is steeped in a solution of tannic acid or material containing tannin; (2) it is passed into a bath of tartar emetic, tin crystals or "iron liquor" (crude ferrous acetate), to fix the tannic acid on the fibre as a metallic tannate; (3) it is introduced into the dye-bath containing as a rule the dyestuff alone, although a little sodium sulphate is sometimes added; the dye-bath is used warm. As examples of basic colours may be mentioned magenta, safranine, rhodamine, auramine, Bismarck brown, chrysoidine, benzoflavine, Meldola's blue, brilliant green and methyl violet. It may be added that the basic colours are sometimes used for "topping" in order to brighten other dyes previously applied to the cotton; such dyes act as mordants for the basic dye. The basic dyes usually give brilliant shades, but in the majority of cases are not fast to light or washing.

(C) **With Acid Colours.**—These colouring matters, which will be more particularly mentioned under wool dyeing, are of small importance in cotton dyeing. Alum and lead acetate are used as mordants in the few cases in which these dyestuffs are employed for cotton.

(D) **With Mordant Dyes.**—These dyestuffs—*e.g.*, logwood, Brazil wood, alizarin, cœruleïn, fustic—need to be used in conjunction with a metallic mordant, such as alum or a chromium salt. The method usually followed consists in impregnating the cotton with the mordant, an operation frequently requiring several baths, and subsequently dyeing in a bath of the dyestuff. Owing to the fact that it is difficult to mordant cotton with metallic salts, especially with chromium salts, the mordant dyes have not been much used until lately, when the introduction of new chromium mordants which are capable of fairly easy application to the fibre, has led to their increased adoption. Turkey red, alizarin red (from alizarin with alumina mordants), logwood blacks with iron, copper and chromium mordants, are the most noteworthy examples of cotton dyeing with mordant dyes. In general the mordant dyes are characterised by yielding colours which are fast to light, washing, &c.

(E) **Dyes of Special Application.**—There are some colours and colouring matters which are dyed on cotton by special processes.

Indigo (see p. 322) will serve as an example. Indigo being insoluble in water is reduced to its soluble derivative hydrindigotin (white indigo, p. 320) by various methods, which are described at p. 322, in order to fit it for use as a dye. The cotton is immersed in vats of indigo thus reduced, and afterwards exposed to the air, when the indigo-white absorbs oxygen and passes into indigo-blue.

The blue got from indigo is characterised by great fastness

to light. Of late years indophenol (p. 303) has been used in conjunction with indigo for the production of blue shades, possessing as it does very similar dyeing properties.

Aniline black is another colour which requires a special process for its production, see p. 311.

A modification of the process for preparing a colour in the fibre itself, which has been already described under direct dyes for cotton (p. 333), may be referred to here. The cotton is first prepared by impregnating it with a solution of beta- or alpha-naphthol, with or without the addition of Turkey-red oil; it is next passed into a developing bath containing the diazo-compound of an amido-body, prepared by acting with sodium nitrite and hydrochloric acid on such substances as para-nitraniline and alpha- and beta-naphthylamine; the colour then rapidly develops. Colours produced in this way are fast to washing, acids and alkalies, and are fairly fast to light. The most important are the scarlet (which is a powerful competitor of Turkey red) from para-nitraniline, the blue from anisidine [the methyl derivative of amidophenol, $C_6H_4(NH_2)O(CH_3)$] and the claret from alpha-naphthylamine. The principal obstacles to the development of this method of dyeing have been the difficulty of preparing the diazo-compound of the amido-body without exercising very great care, and its unstable character when prepared. Recently, however, stable forms of these diazo-compounds have been discovered and utilised —*e.g.*, nitrosamine, azophor red PN.

Metallic compounds are often developed on cotton as dyes; examples are afforded by oxide of iron (buff), oxide of manganese (brown), oxide of chromium (drab) and chromate of lead (chrome yellow and orange). The colours so produced are fast. The method commonly followed for producing these dyes is to impregnate the cloth with a solution of the metallic salt, and to pass it through a bath of such material as will precipitate the required compound on the fibre. A fast brown colour can be similarly obtained on cotton by successive treatment with cutch and bichromate of potash.

Wool Dyeing.—**(A) With Direct Dyes.**—The dyes of this group can be applied to wool, without the use of a mordant, from baths containing salt or Glauber's salt. Sometimes a little acetic acid may be added, in which case the degree of exhaustion of the dye-bath is usually greater than when this substance is omitted. On account of the comparative activity of the constituents of wool fibre, certain dyes yield deeper and faster shades on wool than on cotton. With direct blues the tones of the colour dyed on wool and those on cotton differ, the wool taking a redder tone. Direct dyes are much used for dyeing fabrics made of both cotton and wool ("union goods"). In dyeing such goods it is important to choose those dyes which

have the same, or nearly the same, degree of affinity for the two fibres so that they are dyed nearly the same shade; if there be any difference the cotton should be dyed a little more deeply than the wool. Sometimes by varying the proportion of salt or sodium sulphate in the bath, small differences in the degree of affinity of the dye for the cotton and wool are overcome and a greater evenness of shade is obtained.

The yellow dyes of this group are notable on account of their fastness to light. Certain dyestuffs—*e.g.*, Titan yellow, diamine fast red F and chrysamine—although acting directly, yield faster shades by treatment of the fabric after dyeing with chromium fluoride which acts as a mordant.

(B) **With Basic Colours.**—These are not much used for wool, but deserve comment on account of certain points of chemical interest which they present. Wool has a great affinity for basic dyestuffs, of which magenta is the type, absorbing them from plain baths only. Knecht has shown that, in dyeing wool with this class of dyestuffs, there is an actual splitting up of the colouring matter, the wool fibre exercising its acid functions, liberating the colour base, and combining with it to form a colour lake on the fibre, which is thus dyed, while the acid present in the dyestuff remains in the dye-bath. In this case the dyeing process is a definite chemical operation. The affinity of the wool for the dyestuff is so great that in dyeing a long piece of woollen cloth serious diminution of the strength of the bath takes place before the whole length has been passed through, and the cloth is unevenly dyed. The rapidity of absorption is, therefore, moderated by the addition of 10 to 15 per cent. of sodium sulphate to the dye-bath. Basic dyes for wool are generally used in a hot bath.

(C) **With Acid Colours.**—The acid colours are the most important group of colouring matters for wool-dyeing. Seeing that most acid dyestuffs are sold in the form of their sodium salts, it is generally necessary to add some acid to the dye-bath in order to liberate the colouring matter and allow it to act on the fibre. This necessity may be turned to account for the even dyeing of thick woollen fabrics throughout their mass by first saturating the fabric with the dyestuff alone and then transferring it to an acid bath. By this means the desired dye is formed strictly *in situ*.

The acid dyes may be divided into four groups—(1) Nitro-colouring matters—*e.g.*, naphthol yellow S, aurantia. These require the bath to be acid with sulphuric acid to enable good results to be obtained; they are much used, giving bright and fast colours. (2) Sulphonic acid derivatives of the basic colours, such as acid magenta, acid green, patent blues and thiocarmine. These also require the bath to be acid with sulphuric acid. Many of them are of great value in wool dyeing, as mixing well with other dyes

and enabling a great variety of compound shades—drabs, olives, greens, &c.—to be produced. Indigo extract (*q.v.*) belongs to this class of dyestuffs. (3) Eosine dyes. These do not require a strong acid bath, and acetic acid is, therefore, used with them. They are too fugitive for general use. (4) The azo-colours. These are the most numerous of the acid class of dyes for wool. They may be subdivided into two groups—(*a*) Those dyeing without a mordant. They comprise the oldest and best known —viz., scarlets, ponceaus, oranges, croceines, bordeaux, fast reds, &c. These are dyed in baths made acid with sulphuric acid. Some of the azo-colours are unusually fast to washing and light, and being cheap are extensively used in wool dyeing. (*b*) Those dyeing with a mordant. These are of modern introduction; they are capable of forming colour lakes with metallic mordants, which property appears to depend on the dyestuff containing certain radicles in the same aromatic nucleus in the ortho-position; the groups giving this property are (OH), (COOH) and (HSO_3). The introduction of resorcin, which contains two (OH) groups, into azo-colours imparts to them mordant dyeing properties; a similar quality is observed in dyestuffs containing the group characteristic of a hydroxycarboxylic acid such as hydroxybenzoic or salicylic acid. Lately, dyestuffs, "chromotrops," containing a sulphonic acid of dihydroxynaphthalene, have been introduced, and have the property of forming colour lakes which are distinct in colour from the original dyestuffs. Thus chromotrop 2 R gives a bright scarlet colour on wool, while, when chromed, it yields a deep blue. This class of colours can be used as acid colours after the method described above, but are more generally mordanted. The mordant azo-colouring matters are, as a rule, faster than those dyed without a mordant; they can be applied to wool in one of three ways—(1) The wool is dyed in a bath containing the dyestuff, together with sodium sulphate and sulphuric acid, and then put into a second bath containing the selected mordant—*e.g.*, alum, bichromate of potash and chromium fluoride. This is the best method of employing these colours. (2) The wool may be mordanted first in the usual way and then dyed. This method of working is advantageous when the dyestuffs are used in conjunction with other colouring matters needing a mordant. (3) The dye and the mordant may be used in the same bath if a little oxalic acid be added.

As examples of azo-dyestuffs which are used with a mordant may be mentioned chrome brown, chromotrops, chrome red, chrome yellow, celestine blue, cloth red, cloth brown, diamine yellow, alizarin yellows and diamond yellow.

(D) **With Colours Dyed with a Mordant.**—These are applied to wool which has previously been mordanted with any of the usual mordants. Chromium mordants are generally used as giving faster products. In some rare cases the mordant may

be used after the dye. Occasionally the mordant and the dye are applied in one bath, but this method is wasteful and does not yield the best results. Generally speaking, nothing is added to the dye-baths, but with some of the alizarin colours the addition of a little acetic acid is advantageous. In normal working the dye-bath is started cold and is gradually brought to the boil. In respect of resistance to washing, milling, acids and light, colouring matters dyed on wool with a mordant naturally take a high place. Typical examples of this class of dyestuffs are alizarin, cyanine, galloflavine, alizarin yellow, anthracene brown, gambine, and cœruleïn.

(E) **With Dyes needing Special Application.**—There are very few dyestuffs which are applied to wool by special processes. Indigo has been referred to on p. 322. The alkali blues (p. 290) are dyed on wool by treatment first in a boiling bath containing soda and then in a bath of sulphuric acid. Chromogen I, which is a sodium salt of chromotropic acid, is applied to wool by boiling in a bath containing sodium sulphate and sulphuric acid and then treating the wool in a bath of bichromate of potash.

Silk Dyeing.—In general the methods of dyeing silk resemble those adopted for wool, the two fibres having similar affinities for the various dyestuffs. Silk is rather more difficult to mordant than wool, and, therefore, dyestuffs needing a mordant are not so much used as in wool dyeing. The method of applying a chromium mordant after the dye ("after-chroming"),* which has come into considerable use in wool dyeing, has not been much used in silk dyeing, but merits consideration. The various modes of dyeing silk may be dealt with under the following heads:—

(A) **With Direct Colours.**—Direct colours are much used in dyeing silk, for they possess fairly good affinity for the fibre and give deep and fast shades. They are best dyed from baths which contain phosphate of soda and sometimes a small proportion of soap, and are much used in dyeing half-silk goods—that is, mixed fabrics of cotton and silk. Some of these dyestuffs will not dye silk from a soap bath, while they will dye cotton, so that it is possible to dye cotton-silk goods in two colours, by first dyeing the cotton with a direct dyestuff from a soap bath, and then dyeing the silk with an acid or azo-colour which does not affect the cotton but is readily taken up by the silk. It is obvious that the dye used for the cotton must be such as will resist the acid used in dyeing the silk. Shot effects may thus be obtained on these fabrics.

(B) **With Basic Colours.**—The basic dyestuffs are very extensively used in silk dyeing. They are applied in a boiling bath containing a little sodium sulphate, or more commonly in a bath of old boiled-off liquor (see *Textiles*, Vol. II., p. 265).

* Chromium fluoride is generally used.

This latter method is more particularly applicable where the silk is dyed in the "gum"—that is, where the sericin has not been removed from the silk; in this case the gum in the boiled-off liquor tends to prevent the gum on the silk from being stripped while in the dye-bath.

(C) **With Acid Colours.**—The acid colours are largely used in silk dyeing. They are applied in the same manner as in wool dyeing, or frequently in a bath of old boiled-off liquor or of soap, to which some acid has been added—so-called "broken baths." Silk fibre has a strong affinity for dyestuffs of this class and it absorbs them readily from the dye-bath, giving as a rule good fast shades. The principles underlying the application of these colours to silk are identical with those relating to wool, and are given on p. 336.

(D) **With Mordant Colours.**—Few of these are applied to silk because few mordants adhere well to the fibre. The process commonly used is that of first mordanting and then dyeing the silk. Probably the azo-colours which are commonly dyed with a mordant could be dyed on the fabric first and then fixed with chromium fluoride, but this does not appear to be practised.

(E) **With Dyes requiring Special Processes.**—Indigo is never used as a vat dye for silk. The alkali blues are used in exactly the same way as for wool. No other dyestuff belonging to this division is applied to silk dyeing.

Jute Dyeing.—The dyeing of jute in some respects resembles the dyeing of cotton, but there are important differences. Direct colours can be applied by the same processes as those used for cotton, and they give good results. Basic colours can be dyed on jute from a plain boiling bath. On account of the chemical activity of jute fibre, exceeding that of other vegetable textile materials, dyeing can be effected by the direct interaction of the dyestuff and the fibre in the manner which obtains with wool and silk, thus affording evidence that the dyeing in this case is a definite chemical process.

The azo-colours can be applied to jute from baths containing alum, which forms a colour lake with the dyestuff and fixes it on the fibre. The mordant colours may be used in the same way as for cotton.

Linen and other vegetable fibres consisting essentially of cellulose are dyed in precisely the same way as cotton. Animal fibres are dyed in the same way as wool or silk.

The production of coloured mixed fabrics—*e.g.*, those composed of any mixture of cotton, wool and silk—is effected in the simplest case by using the appropriate yarns previously coloured. For dyeing in the piece, colouring matters which behave as substantive dyestuffs for both animal and vegetable fibres, such as the benzidine and the diazo-dyes generally, are freely used when a uniform colour is required. The wool may

also be first dyed with an acid dyestuff and the fabric mordanted with tannin and tartar emetic, as usual for dyeing the cotton of the fabric. Mixed shades may be produced in a similar manner, but with the difference that dyestuffs differing in colour are used for the two kinds of fibre to be dyed. Thus the wool may be dyed with fast red, and the cotton (mordanted with tannin and an antimony salt) with methylene blue.

(C) **PRINTING.**—The object of colour printing on textile fabrics is to produce a coloured pattern on a white ground, or *vice versâ*, without weaving the design. Two methods are adopted for this purpose, the older being known as "**block printing**," and the more modern as "**roller printing.**"

In block printing the design is engraved on a large wooden block, the lines of the design standing up. The colour is spread over the block, which is then impressed on the cloth to be printed. In roller printing the design is engraved in, or on, a copper roller, which is inked by another roller with the colour to be applied. The cloth is made to pass between the engraved roller and a large roller known as a "pressure bowl," and thus receives the desired impression. Every colour of the design requires a separate roller.

Just as it is necessary that printing ink should be of pasty consistency in order that it may cling to the type and not run on the surface of the paper, so it is requisite to apply a thickening agent to colours to be used in printing textile fabrics. As thickening agents are used such bodies as starch, gum and dextrin (*q.v.*). The same dyestuffs and mordants are employed in printing as in the dyeing of textile fabrics. Apart from the question of choosing suitable dyestuffs and mordants, there are various methods of obtaining printed designs on fabrics, which are used according to the precise effect or "style" sought to be produced by the printer. The character of the fibre has some influence upon the methods used. Cotton cloth is the fabric on which printing is mostly done; of late years printing on silk and wool has greatly increased, but is still less practised than calico-printing.

Five methods or "styles" may be distinguished; they are—(1) Steam style; (2) Pigment style; (3) Dyeing style; (4) Discharge style; (5) Resist style.

(1) **Steam Style.**—This style consists essentially in printing with a paste composed of the dyestuff, mordant and thickening agent, and steaming the fabric bearing the impression.

With basic dyestuffs tannic acid is commonly used as a mordant, and the fastness of the colour may also be enhanced by passing the fabric, after steaming, through a bath of tartar emetic or other antimony salt.

In order to prevent a too rapid action between the dyestuff and the mordant, acetic acid is usually added to the printing

paste; this is driven off on steaming and the colour is thus fixed. After steaming, the goods may be passed through a soap bath to remove the thickening agent. This method is applied to almost all colours that the calico-printer may use.

(2) **Pigment Style.**—In this style of calico-printing pigment colours—*e.g.*, Prussian blue, Guignet's green—are used. They are in no sense dyed on the fabric, but are caused to adhere by means of some fixing agent. Blood albumin is the material generally employed for this purpose. The colouring matter is mixed with a thickening agent and the required quantity of albumin; the cloth is then printed, steamed and finished by soaping and washing. The steaming coagulates the albumin, thus fixing the colour on the fabric. Synthetic dyestuffs available for use in printing are now so numerous that mineral pigments are less frequently required than formerly, and this style of printing, which is especially fitted for the latter class of colouring matters, is practised to an extent correspondingly smaller.

(3) **Dyeing Style.**—In this style or method of working a mordant mixed with a thickening agent is printed on the fabric and fixed by steaming, or frequently by passage through baths of alkaline salts, such as carbonate, phosphate or arsenate of soda. The printed material is then introduced into a bath containing the dyestuff which is to be used; the dye is thus fixed only on those parts of the fabric where the mordant has been printed. When the colour has been fully developed, the cloths are finished by soaping and washing, and sometimes by clearing with a bath of chloride of lime to remove any colour from the white portions of the fabric. This method is commonly practised in printing with alizarin, aluminium sulphocyanide and chromium acetate being used as mordants. The process is not so much used now as formerly, the steam style giving similar results with greater ease of working. Only a limited number of colours can be obtained by this method.

(4) **Discharge Style.**—The principle of this method consists in dyeing the cotton cloth and then printing it with a substance capable of destroying the colour which has been dyed, thus giving a white pattern on a coloured ground. When direct colours are used, the cloth is first dyed in the usual way, and a pattern is produced by printing on a discharge paste containing some powerful reducing agent—*e.g.*, zinc dust, bisulphite of soda, stannous chloride or stannous acetate. On steaming and washing, the colour of the printed portion is discharged and a white design on a coloured ground is obtained. Coloured designs on coloured grounds may be produced if some colouring matter on which the discharge has no effect is added to the discharge paste used for printing. Colouring matters capable of yielding colourless soluble products when reduced

—*e.g.*, the azo-dyestuffs which give so-called leuco-compounds under such conditions—can be utilised in this manner. An extension of the principle of the discharge method is possible for dyestuffs of a different class. Thus, with mordant dyes—*e.g.*, alizarin—it is usual to discharge the mordant and thus prevent the fixation of the dyestuff. In this case the method consists in impregnating the cloth with the mordant (chromium acetate, for example) and then printing with a discharge paste containing sodium citrate, which on subsequent steaming, renders the mordanting oxide soluble, so that when the piece is passed through the washing bath, the mordant is dissolved away wherever the discharge has been printed. On subsequently dyeing the cloth with the dyestuff, the latter is taken up on those parts where no discharge has been printed and a coloured pattern is thus produced.

For indigo-dyed cloths an oxidising discharge is used. A discharge paste, made from bichromate of potash or bichromate of soda and a thickening agent, is printed on the cloth, which is then passed through a bath containing sulphuric acid and oxalic acid;* the chromic acid thus liberated oxidises the indigo and discharges its colour. Coloured designs may be produced by adding to the discharge paste pigment colours (such as chrome yellow, vermilion and Guignet's green), which are not affected by the chromic acid or the discharge acids. When these pigments are used albumin is commonly added to the discharge paste for the purpose of fixing the colours on the cloth. An alkaline solution of a ferricyanide is also used as an oxidising discharge for indigo.

(5) **Resist Style.**—This may be regarded as the converse of the discharge method. It is carried out by printing on the cloth a **resist**—*i.e.*, a substance which will prevent the fabric from fixing either the mordant or the dyestuff in the bath which follows. Such resists are either mechanical or chemical in their action. To the first type belong oily matters—*e.g.*, resins made into a paste with pipeclay or similar mineral matter—the fabric being thus protected in the dye-bath; the resist can be subsequently removed by a suitable solvent. Chemical resists consist of such compounds as sodium citrate or citric acid, which have the property of preventing the precipitation of many hydroxides or basic salts from aluminium salts, iron salts, &c., so that these cannot act as mordants in places where the citrate has been applied. Such resists to the dyestuff (which may be also regarded as discharges of the mordant) have been dealt with in section (4).

Wool Printing.—Of late years considerable development has taken place in the printing of woollen fabrics. A greater variety of colouring matters can be used than in the printing of cotton,

* Acting in this case as an acid, and not as a reducing agent.

and the processes are usually somewhat simpler. The woollen cloth is prepared by treatment first in a bath of chloride of lime, and then in one of hydrochloric acid, the wool acquiring in this way a greater affinity for synthetic colours, especially those of acid dyeing groups. Steam and discharge styles are chiefly used for wool. In the steam style the colouring matter in the form of a thickened solution is printed on the cloth, which is then steamed, washed and dried. The direct and basic colours do not require any addition to the printing paste, while the acid colours require the addition of a small quantity of some acid —*e.g.*, oxalic, tartaric or sulphuric acid. When mordant colours are used in wool printing, aluminium acetate or chromium acetate is generally added to the printing paste. The discharge style is carried out by dyeing the wool with a suitable colour, and then printing on a discharge paste containing a reducing agent such as stannous acetate. The rationale of the process has been described under cotton printing.

Silk printing is carried out similarly to wool printing.

Water for Dyeing.—Except for special cases which have been already noted, the softer a water the better it can be used for dyeing purposes, and even where lime salts are desirable the addition of these to a pure water is preferable to the use of a water naturally hard and containing other salts. In general, all salts of lime and magnesia, even those remaining in solution on boiling the water *per se*—*e.g.*, $MgCl_2$, $Ca(NO_3)_2$—are objectionable since they tend to precipitate the dyestuff from the bath. Traces of iron are liable to have a saddening effect on the colours (see above). In the preliminary and subsequent processes of washing, much waste of soap is occasioned by the use of a hard water (see Vol. I., p. 108); in short, systematic softening is always remunerative in dyeing and cognate industries.

CHAPTER XIV.

PAPER AND PASTEBOARD.

Typical paper consists of fibres of approximately pure cellulose matted together to form a sheet. The cellulose employed may be either that existing as fibres used for making vegetable textiles—*e.g.*, cotton and linen—in the form of rags of these materials, or that present, together with much cementing substance, in wood. Paper for many purposes, however, is usually "loaded" with mineral matter, such as kaolin, to produce a smooth non-porous surface fit for writing upon. The main sources of cellulose for paper making are rags (linen and cotton), esparto, flax in the form of spinner's waste, hemp in the form of old ropes, wood, straw and jute. Old paper is also reworked. Whatever the source of the cellulose, it has to be reduced to pulp, and where it is cemented together in the raw material the cementing substance must be removed before the pulping. A bleaching process is also generally necessary. The finest papers are made from linen rags; in the first stage of the manufacture the rags undergo a preliminary dusting from adhering rubbish, and are then boiled in the manner subsequently described for esparto, but in a less drastic fashion. A washing from alkali and bleaching with chloride of lime follow, and the rags are finally thoroughly pulped, during which stage the "loading"* (if any), colouring matter and size are introduced. When a sizing of resin in the form of aluminium resinate is adopted, it is added at this stage, as a mixture of sodium resinate and alum, which react to form sodium sulphate and aluminium resinate. (When an animal size (gelatin) is used, the finished paper is passed through a solution of gelatin to which alum has been added.) The colouring matter employed is generally some form of blue, usually ultramarine to correct the yellow tint of the fibre. To make the pulp or magma into a sheet of paper, a frame, on which wire cloth is stretched, is passed through the water in which the pulp is suspended, and a film of pulp of the required thickness thus removed. The sheets formed in this manner are pressed between felt, passed through a solution of

* The usual mineral additions to paper are kaolin (*China clay*), barium sulphate (*blanc fixe*), calcium sulphate (*gypsum, annaline, pearl hardening*), and magnesium silicate (*soap stone, steatite*).

gelatin (*v.s.*) and dried and pressed by being passed between heated rollers (**calendering**). It will be seen from the foregoing brief description, that paper-making from rags is mainly a mechanical process. The chief manner in which chemistry is concerned with paper-making is in the preparation of approximately pure cellulose from crude cellulose—*e.g.*, wood.

In making paper from esparto, which contains about 50 per cent. of cellulose, the raw material has to be picked to remove dirt, and boiled with about 10 per cent. of caustic soda in **kiers** (large boilers) under a pressure of 10 to 50 lbs. of steam. The esparto is carried on a false bottom in the kier, the liquor is run in and the steam turned on; the steam is admitted below the false bottom, where it accumulates, forcing up the liquor through a central pipe and causing it to impinge against a dome, from which it is reflected on to the esparto. This treatment with alkali is more severe than is necessary for rags, as the esparto contains resin which has to be removed. The spent alkaline liquor is nearly black in colour from the presence of much resin soap; the alkali may be recovered from it by the method described below. Washing and bleaching finish the chemical part of the treatment. Straw, jute and other like materials are similarly treated as far as chemical processes are concerned.

The preparation of wood involves the removal of more strongly adhering cementing matters than those present in esparto, so that yet more depends on the proper conduct of the chemical treatment, though for the commonest paper, or for use as a filling material, "**mechanical wood pulp**"—*i.e.*, wood which has been ground and its fibres thus separated—can be used. Such mechanical wood pulp is of short fibre and felts badly, and, moreover, as it contains lignin, becomes yellow or brown on exposure to sunlight.

Several chemical methods can be used for the treatment of wood fibre. Thus the wood is cut into slices $\frac{1}{2}$ inch thick, across the grain, knots and other imperfections being removed, and is digested with caustic soda solution (20 per cent. of the weight of the wood) under pressure at a temperature of about 160° C. = 320° F., during which process the matter other than cellulose is dissolved, and a portion of the cellulose itself is destroyed. The residual cellulose, which retains the form of the original pieces of wood, is broken down to a pulp, freed from the alkaline liquor, washed, bleached with chloride of lime and sulphuric acid, and made into paper. Formerly the whole of the alkaline extract was run to waste, but now it is evaporated in multiple evaporators, ignited, and the crude sodium carbonate (containing sodium silicate in cases where siliceous raw materials —*e.g.*, straw, have been used), resulting from the decomposition of the sodium salts of organic acids, re-causticised and used again. Recently it has been proposed to obtain acetic acid from the

residue got by charring spent lye from this process, which in the case of esparto contains sodium acetate to the extent of about 6 per cent. of the weight of the raw material.

The multiple evaporator mentioned above consists of a series of 3 or 4 vessels (Fig. 39) into the first of which, A, the alkaline liquor is admitted through the pipe B, and steam at 40 to 50 lbs. pressure through the pipe C. The liquor flows up the pipes *a*, *a*, *a*, around which the steam circulates. The vapour from the liquor passes through the pipe D into the steam chamber of the second vessel E, which also receives the waste heat from the

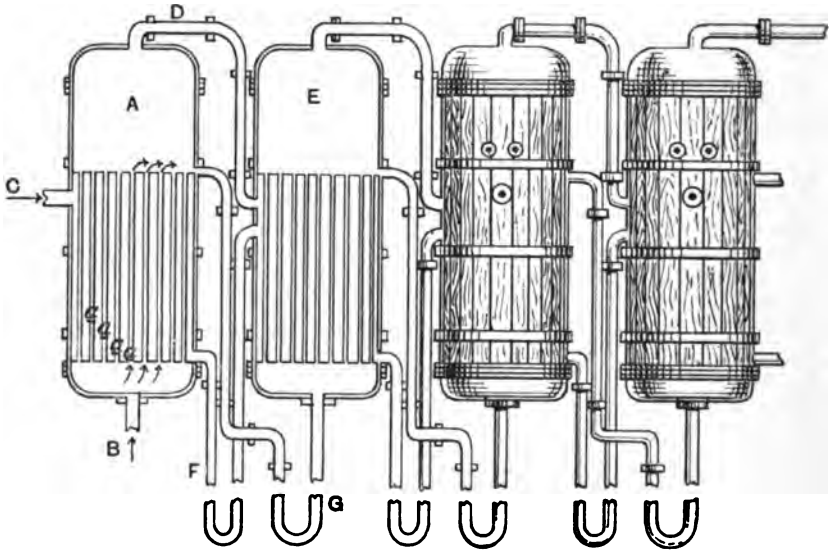


Fig. 39.—Multiple evaporator.

A, First evaporating vessel; B, pipe for liquor; C, pipe for steam; *a*, *a*, *a*, steam heated pipes; D, pipe for vapour of liquor; E, second evaporator; F, steam connecting pipe; G, pipe connecting evaporators.

steam chamber of the first vessel through the pipe F, which is 30 feet or more in length, so that the steam on its passage is condensed to water and re-evaporates under reduced pressure. The operation is repeated in the succeeding vessels, a vacuum being maintained at the liquor chamber of the last vessel by means of a pump and surface condenser. With regard to the circulation of the liquor itself, it flows from one evaporator to the next by means of a pipe, G, also dipping 30 feet below the level of the vessels.

A cheaper reagent than caustic soda for the chemical treat-

ment of wood is sodium sulphide, which is used in a similar manner. It is generally made *in situ* by starting with a mixture of sodium sulphate and lime, and evaporating the liquor after it has extracted a certain quantity of cementing matter, which on ignition reduces some of the sulphate to sulphide, and yields a mixture of sodium sulphide and caustic soda. The yield of wood pulp by the caustic soda process is about 30 to 35 per cent. of the wood used, one-third or more of the total cellulose originally present being destroyed.

Inasmuch as the action of caustic soda is hydrolytic, it is possible to substitute dilute acids for the alkali. A more recent method of preparing wood pulp is that known as the sulphite process. The comminuted wood is digested with a solution of calcium or magnesium bisulphite (3 to 5 per cent. of SO_2) at about 160° C. = 320° F. in lead-lined digesters. Before the digesters are closed, the air is expelled by steam. The bisulphite is produced by passing pyrites kiln gases up a tower filled with limestone, dolomite or magnesite, down which a stream of water flows. The constitution of wood lends itself to the formation of certain organic sulphur acids (sulphonates), which fact doubtless facilitates the separation of the cementing material, and probably also aids the hydrolytic action which is necessary. The spent sulphite liquor is bright yellow, and contains much resin, tannin and acetic acid, together with products of the hydrolysis of cellulose—viz., various sugars. No successful utilisation of sulphite liquor has yet been achieved. The yield of wood pulp is greater than by the caustic soda process, amounting to 40 to 50 per cent. of the dry wood, the destructive action on the cellulose being less severe. Sulphite pulp is fairly light in colour, but is usually bleached, a good deal of chloride of lime being necessary in order to oxidise the reducing substances present.

CHAPTER XV.

PIGMENTS AND PAINTS.

THE necessity for a protective coating on structures intended to be permanent has given rise to the custom of applying some form of paint, which is simply a thin layer of oily or resinous matter, containing finely-divided solid material in suspension.

The nature of the solid substance is determined by several considerations—*e.g.*, its power of absorbing and reflecting light, resisting corrosive influences, and gratifying the æsthetic instinct. Such solid substances are termed **pigments**, in contradistinction to their admixtures with a vehicle — *e.g.*, linseed oil—which are called **paints**. The colour of a pigment depends on the wave lengths of the light which it reflects; few pigments reflect light of only one wave length, or even of approximately equal wave lengths, whence it follows that the colours of most pigments are impure, and are found, on spectral analysis, to contain more than one colour of the spectrum. Mixtures of pigments, therefore, do not affect the eye in the same way as do similar mixtures of the colours of the spectrum —*e.g.*, a mixture of a blue and a yellow pigment is commonly green, but one of blue and yellow light is white. This arises from the fact that in a mixture of pigments the light suffers an absorption by each pigment successively, and it is only that portion of the light which is not absorbed by any of the pigment which reaches the eye and communicates to it a particular sensation of colour. In the case of blue and yellow pigments, the light reflected by each always contains green, which is not absorbed to any great extent by either, and thus the net result is that the mixture appears green. The **body** of a pigment is its **covering power**, or property of hiding a surface to which it is applied. This quality chiefly depends on (1) the fineness of the particles of the pigment, and on (2) the opacity of these particles—*i.e.*, their tendency to reflect or absorb, and fail to transmit, the greater portion of the light. "Body" is usually judged by a comparative trial with a pigment of known excellence in covering power, when the pigment is made into a paint. Thus white lead serves as a standard for white pigments.

(A) MINERAL PIGMENTS.

1. **WHITE PIGMENTS.—White Lead.**—This substance is the best white pigment known, in respect of its covering power and colour. It is, however, readily darkened by exposure to air containing sulphuretted hydrogen, and is somewhat costly. It also possesses the disadvantage that its manufacture is attended by a certain amount of risk of lead poisoning to the operatives. Chemically, white lead is basic carbonate of lead, approximating in composition to the formula $2PbCO_3.Pb(OH)_2$. Many lead pigments, consisting of neutral carbonate, or even of lead sulphate or oxychloride, are fraudulently termed white lead. The older methods, and those which are still claimed to produce white lead of the finest quality, depend upon the ease with which lead, in the presence of acetic acid and air, becomes converted into lead acetate, and subsequently basic lead acetate, and upon the facility with which this substance can be converted into white lead by the action of carbon dioxide. The best product is obtained when this cycle of changes is conducted without any of the reactions taking place in solution in large volumes of water—*i.e.*, when the process used is not one of those known as "precipitation methods."

The Dutch or Stack Process.—This old and empirical process yields the best white lead. In this method sheets of pure lead* 2 feet × 4½ inches × ½ inch are rolled into a coil (see Fig. 40), which is placed in an earthenware pot provided with a shelf (see Fig. 41), upon which the lead rests, and containing weak

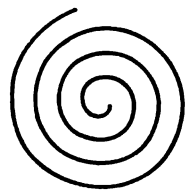


Fig. 40.—Coil.

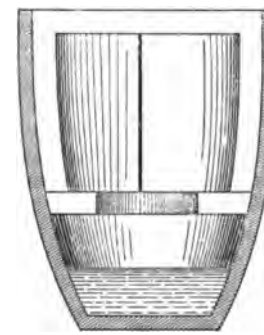


Fig. 41.—Pot, with Shelf.

vinegar. Many such pots are built up into "stacks," and are surrounded by horse dung, the whole being covered up with the same material. A single stack will contain as many as 12,000 pots.

* The purity of the lead is important, as the presence of traces of copper and antimony is found to cause the production of white lead of inferior colour.

In the English process the lead is used in the form of grids or gratings, and the dung is replaced by spent tan. The former is rather liable to cause the discolouration of the white lead by the evolution of sulphuretted hydrogen. The dung or tan speedily ferments, the temperature of the heap consequently rising to 60° C. = 140° F., and evolves CO_2. Under these conditions the acetic acid of the vinegar is volatilised, and in conjunction with moisture and oxygen of the air, corrodes the lead, with the ultimate formation of basic lead acetate, which is then decomposed by carbon dioxide, produced by the fermentation of the dung. The first of these changes may be represented by the equation—

$$(1)\quad Pb_3 + O_2 + 2CH_3CO_2H + H_2O = \underset{\text{Basic lead acetate.}}{(CH_3CO_2)_2Pb.2Pb(OH)_2}$$

The second change may be represented thus—

$$(2)\quad 3[(CH_3CO_2)_2Pb.2Pb(OH)_2] + 4CO_2 = \underset{\text{Lead acetate.}}{3(CH_3CO_2)_2Pb} + \underset{\text{White lead.}}{2[2PbCO_3.Pb(OH)_2]} + 4H_2O.$$

The lead acetate thus liberated is reconverted into basic lead acetate in contact with metallic lead, oxygen and water, the product serving again for the production of white lead. Thus the same portion of acetic acid suffices for the corrosion of an indefinite quantity of lead. After a period varying from eight weeks to three months, the heap is dismantled, and the coils are found to be incrusted with "corrosions" of white lead. The white lead is knocked off and taken to the mill, where it is ground and washed to remove lead acetate, dried, and put on the market. The residual unattacked lead, amounting to from 30 to 50 per cent. of the weight of the lead originally taken, is known as "blue lead," and is remelted and used again.

The German or Chamber Method.—This differs in principle from the stack method in that the carbon dioxide is supplied from an external source—viz., a coke fire (which serves also to keep the temperature of the corroding chamber at about 35° C. = 95° F.)—instead of being produced by fermentation on the spot. The acetic acid is also introduced from without, weak vinegar being distilled from retorts outside the chamber. This is built of brick, and contains shelves upon which the sheets or gratings of lead are disposed. The supply of carbon dioxide, acetic acid and water vapour has to be carefully managed, lest the product be granular instead of soft and amorphous, or contain too much lead oxide, which imparts to it a yellow tint. The process may take from eight to ten weeks for completion, though this time may be considerably shortened in modern practice. It has been proposed to hasten the corrosion of the lead by covering the shelves in the chamber with a metal, such

as tin, electronegative to lead, the galvanic couple thus set up promoting the reaction.

Precipitation Processes.—The principle underlying the majority of these is the formation of basic lead carbonate (white lead) by treatment of basic lead acetate with carbon dioxide, the reaction being similar to the final change taking place in the dry process described above (equation 2).

In the **French or Clichy process** litharge is heated in a solution of neutral lead acetate, and the solution of the resulting basic lead acetate is separated by decantation from undissolved lead, copper and other impurities which occur in litharge, and treated with carbon dioxide from a lime kiln, in a vessel provided with numerous delivery pipes to distribute the stream of gas. The carbon dioxide is freed from sulphur dioxide and similar impurities by being washed with water previous to its entering the precipitating vessel.

The neutral lead acetate produced by the precipitation of white lead from basic lead acetate (p. 350) is pumped back into the first vessel of the series and used for dissolving a further quantity of litharge, thus going through the cycle of changes repeatedly.

A method which avoids the use of lead acetate is Milner's process. This consists in producing a basic chloride of lead by treating litharge with a solution of common salt, the mixture being continually agitated for several hours. The proportions used are 1 of litharge, 4 of salt, and 16 of water. The reaction induced speedily causes these to set to a pasty mass, consisting of basic lead chloride and caustic soda. The change occurring may be thus represented—

$$4PbO + 2NaCl + 5H_2O = PbCl_2.3PbO.4H_2O + 2NaOH.$$

This mass is transferred to a lead-lined iron cylinder, into which carbon dioxide is forced under pressure, the contents of the cylinder being kept stirred by agitators. The carbon dioxide is prepared and purified as described under the Clichy process. The reaction occurs on the following lines:—

$$3[PbCl_2.3PbO.4H_2O] + 6NaOH + 8CO_2 = 4[2PbCO_3.Pb(OH)_2] + 6NaCl + 11H_2O.$$

Chemically considered, the reaction is analogous to that in which acetic acid is used as a corroding agent, the function of the salt being to induce the union of lead with oxygen, water and carbon dioxide, a reaction which only takes place directly at a slow rate, because of the insolubility of lead oxide. Other salts than those mentioned above have been proposed as intermediaries in the formation of basic carbonate of lead from metallic lead or litharge —*e.g.*, the basic nitrate, and a solution of litharge in caustic soda. In another series of processes the precipitation of basic

carbonate of lead is effected by the use of sodium carbonate instead of carbon dioxide. The many processes for the manufacture of white lead which have been devised may be attributed to (1) the slowness of the old corrosion methods and (2) the occurrence of cases of lead poisoning among operatives employed in the manufacture of white lead by these processes. The first objection to the corrosive methods appears to be insuperable; it must, however, be noted that no product of more rapid methods is equal in covering power to white lead made by the old slow stack process. The second can be met by proper use of respirators and soap.

White lead of good quality approximates in composition to the basic carbonate already mentioned, and therefore contains 86·3 per cent. of PbO, 11·4 per cent. CO_2, and 2·6 per cent. of H_2O. It is put on the market both dry and "ground"—*i.e.*, ground in linseed oil to a stiff paste—for convenience in mixing to a thin paint with boiled linseed oil and oil of turpentine. The quantity of linseed oil present is about 6 to 8 per cent. It was formerly supposed that a portion of the oil was saponified by the lead hydroxide of the white lead, and thus caused a more permanent association of the pigment with its vehicle, but this view is now discredited. On account of its comparatively high price (£20 per ton), white lead is largely adulterated with barium sulphate (barytes), lead sulphate and calcium carbonate.

Other White Pigments Containing Lead.—In most cases these are lead sulphate, alone, or mixed with such diluents as barium sulphate. These are made either by precipitating a salt of lead—*e.g.*, the acetate—with sulphuric acid, or by taking advantage of the ease with which galena (PbS) is converted into lead sulphate ($PbSO_4$) when roasted in air at a moderate temperature. The action that occurs is probably the formation of lead oxide, which is moderately volatile, and sulphur dioxide, the two substances being carried off together as lead fume, and uniting in the presence of oxygen to form lead sulphate. Crude lead fume contains lead oxide and metallic lead, as well as lead sulphate, and has to be further roasted to lead sulphate, any residual grey tint due to impurities being removed by treatment with sulphuric acid. According to Hurst the finished pigment, so-called "sublimed white lead," contains—

	Per cent.
Lead sulphate,	82·5
Lead oxide,	0·5
Zinc oxide,	6·3
Lead carbonate,	9·4
Water,	1·3
	100·0

The presence of zinc oxide is due to the existence of zinc in

many lead ores (the volatility of zinc causing it to concentrate in the fume), and adds to the value of the pigment.

A chlorosulphite of lead is made by oxidising lead sulphide (galena) or a mixture of lead fume with pyrites, with air only sufficient to convert it into sulphite, and treating this in the chamber, into which it is blown, with hydrochloric acid gas generated by spraying brine into the flame of the furnace. This is known as "**Caledonian White Lead**," but, for the reasons stated above, it is not true white lead, to which it is inferior in covering power.

Zinc White.—Ordinary zinc white consists of zinc oxide. It is generally prepared by distilling zinc into large chambers, where the vapour comes in contact with air and burns, the resulting zinc oxide being deposited on the sides of the chambers, from which it is afterwards collected. It may also be prepared directly by heating the roasted ore with coke or anthracite, and burning the vapours of zinc thus obtained. This method is less common than the previous process, as cadmium is even more volatile than zinc, and its oxide, being brown, discolours the product, while in the preparation of metallic zinc (see Vol. I., pp. 183, 185) cadmium is eliminated.* Another plan consists in extracting crude zinc oxide with ammonium carbonate, the impurities—*e.g.*, lead and cadmium oxides—being left undissolved, and distilling off the ammonium carbonate; the residual zinc carbonate is then ignited to oxide.

Zinc white has poor covering power, but has the advantage of not being blackened by sulphuretted hydrogen unless the pigment contain lead, as it almost invariably does in its commercial form. It is liable to adulteration with barium sulphate, kaolin and whiting.

In order to obtain a pigment as permanent as zinc white, but possessed of greater body, other zinc compounds, notably the sulphide, have been used. "**Orr's zinc white**" is a mixture of barium sulphate and zinc sulphide, prepared by precipitating a solution of zinc sulphate with barium sulphide. Unlike ordinary zinc white, it is free from lead.

Barytes (*barium sulphate*).—This substance is chiefly used as an adulterant for other pigments. It is either prepared by grinding and levigating the mineral barytes (crude barium sulphate)—the dark colour due to iron and other impurities being removed by treatment with sulphuric acid, and the tint of the washed product improved by the addition of a little ultramarine—or is made by precipitating the solution of a barium salt with one of a sulphate. Precipitated barium sulphate is a bye-product in many industries. It has a greater covering power

* Some samples of zinc white are tinged yellow by the presence of a minute quantity of cadmium sulphide; their colour can be improved by roasting the sulphide to oxide, which is a less powerful pigment.

than has the native material, which is more coarsely crystalline in structure.

Whiting.—Whiting is simply levigated chalk, and is used as an adulterant and diluent for other pigments, and for preparing whitewash, which is whiting suspended in water by the aid of a little size.

2. **BLUE PIGMENTS.—Ultramarine.**—In former times a costly blue pigment was obtained by grinding a comparatively rare mineral, **lapis lazuli**, consisting chiefly of silica, alumina, soda and sulphur, to an impalpable powder. The same pigment is now cheaply prepared by heating together china clay, sodium sulphate or sodium carbonate, carbon and sulphur, the use of these materials having been first suggested by analyses of the mineral. The carbon is necessary to reduce the sodium sulphate to sulphide. The china clay must be approximately pure kaolin, $Al_2O_3.2SiO_2.2H_2O$. The soda used, now generally sodium carbonate, must also be as nearly pure as possible. The proportions in which the materials are mixed vary according to whether it is desired to make "soda-ultramarine" poor in silica, or soda-ultramarine rich in silica. A third variety, "sulphate-ultramarine," is still prepared from sodium sulphate. Soda-ultramarine poor in silica is made, for the sake of its darker and richer hue, from a mixture of the following composition :—

Kaolin, ...	100 parts.
Na_2CO_3, ...	100 ,,
C, ...	12 ,,
S, ...	60 ,,

That rich in silica is prepared from a mixture containing

Kaolin, ...	90 parts.
Free silica, ...	10 ,,
Na_2CO_3, ...	100 ,,
C, ...	12 ,,
S, ...	60 ,,

In the manufacture, as carried out at some works, it is advantageous to prepare first a **green ultramarine**, which can either be marketed as such or converted into **blue ultramarine** by re-heating with sulphur. Where blue ultramarine is alone required it can be made by one heating, the process being, therefore, called the "direct" process. For the production of green ultramarine the mixture is packed into small crucibles about 6 inches in height and 4 inches in diameter. These are covered and placed in a furnace consisting of a chamber over a fire grate. Care is taken to exclude air, and the temperature is raised to redness. This takes from 8 to 12 hours, after the elapse of which time the furnace is allowed to cool as slowly as possible, and the contents of the crucibles washed and ground, then constituting green ultramarine. In

view of the fact that the colour depends on the presence of sulphur, great precautions must be taken to avoid oxidation during this heating. To convert this into blue ultramarine it is heated with sulphur, with access of air, at a low temperature, in order to convert a portion of the sodium of the green ultramarine into sodium sulphate, the difference in colour arising from the alteration of the quantity of sodium present as an essential part of the pigment, green ultramarine containing nearly twice as much as blue. This second heating is generally conducted in a muffle, on the floor of which the green ultramarine is spread. The final process of finishing the ultramarine is the same as that which is used for ultramarine made by the direct process (*v.i.*). For the direct production of blue ultramarine, the mixture given above is packed into muffles, which are closed and heated in sets in a muffle furnace for several weeks at a moderate red heat, the end of the process being judged by the withdrawal of a sample from time to time. The access of air to the mass is small in this method of heating, but, nevertheless, is sufficient to destroy the blue colour of the outer layers. The intermediate layers are a good blue, while the centre of the mass has a green tint from defect of air. For more rapid working crucibles are preferred, the process being then conducted very much as was described for green ultramarine. The crude blue ultramarine is a fritted blue mass, and contains soluble sodium salts (chiefly sodium sulphate) which must be removed by grinding under water and thorough washing. The ultramarine is graded by levigation, the most finely divided being reckoned best. Ultramarine is a pigment very stable under ordinary influences, but is easily bleached by acids, which decompose it completely, evolving sulphuretted hydrogen and depositing sulphur. This property gave rise to the supposition that the compound contained some sulphide or polysulphide of sodium.

The cause of the colour of ultramarine has been much debated. Recently, Knapp has put forward the view that it is due to the presence of a peculiar modification of sulphur, very similar to the "black" sulphur obtained by heating a mixture of sulphur and oil. Under many conditions this allotropic modification of sulphur becomes blue, particularly when spread over a large surface. Such a surface would be supplied by the silicates in ultramarine, and, when these are attacked by an acid, the blue sulphur would become ordinary yellow sulphur. Bodies of composition corresponding with that of ultramarine, but containing other bases in place of soda, have been prepared—*e.g.*, potassium and silver ultramarine—which are blue and yellow respectively. Different samples of ultramarine vary in composition according to the mode of manufacture, which is regulated by their intended use. The difference between blue and green ultramarine is shown by the following figures:—

	Blue.	Green.
SiO_2,	40·9	38·5
Al_2O_3,	24·1	29·0
S,	14·0	8·5
SO_3,	3·0	...
Na_2O,	15·5	23·7
H_2O,	2·5	...

Besides its use as a pigment, in the ordinary sense of the term, ultramarine is frequently employed for correcting any slight yellow tint in goods which should be white—*e.g.*, barium sulphate, sugar, starch and paper; it is also used in making factitious mottled soaps (see Vol. II., p. 248), and in calico-printing.

Prussian Blue.—This pigment is essentially composed of iron, carbon and nitrogen, and in its best form is the ferric salt of hydroferrocyanic acid, $H_4Fe(CN)_6$, so that its formula may be written $Fe_4[Fe(CN)_6]_3$, although the commercial product varies considerably from this composition, and frequently contains potassium in the form of a double cyanide of that metal and iron. Potassium ferrocyanide (yellow prussiate of potash), K_4FeCy_6, is the raw material for the ferrocyanogen group. It is no longer made by the manufacturer of Prussian blue, the trade of making cyanides being now distinct (see *Minor Chemical Manufactures*, Vol. II., Chap. XVIII.).

Prussian blues of somewhat different shades are made from potassium ferricyanide (red prussiate of potash), K_3FeCy_6.

The best and purest variety of Prussian blue is known commercially as **Chinese blue**, and is made by mixing a solution of ferrous sulphate ("copperas"), containing 1 cwt. to every 30 gallons of water, and 10 lbs. of sulphuric acid with a solution of potassium ferrocyanide of equal strength. This dilution is advantageous as giving a finer precipitate than would be obtained in stronger solutions. The precipitate is white at first, being ferrous ferrocyanide, Fe_2FeCy_6, but on account of the presence of dissolved oxygen and of ferric sulphate in commercial copperas, it is frequently light blue owing to the formation of some ferric ferrocyanide. The precipitate is allowed to settle, the clear liquor run off, and the precipitate oxidised to ferric ferrocyanide by treating it with any convenient oxidising agent, bleaching powder (made into a thin cream with water) being the cheapest; nitric acid is preferred on the Continent; air would probably be cheaper than either of these, but it is found that the colour of the product is not so good. After the addition of the bleaching powder, dilute hydrochloric acid is added; chlorine is thus evolved, and oxidises the ferrous ferro-

cyanide to Prussian blue. Sometimes the bleaching powder is used to oxidise the ferrous sulphate into ferric sulphate previously to precipitation, but the blue thus prepared is not of equally good tint. By substituting potassium ferricyanide for the ferrocyanide, a blue of redder tint than that produced by the latter is obtained. The blue is washed and pressed into cakes. Common Prussian blues are either prepared by oxidising ferrous ferrocyanide by air, or by the addition of diluents such as barium sulphate, chalk, &c., to ordinary Prussian blue. If in the preparation of Prussian blue potassium ferrocyanide be kept in excess—*e.g.*, by pouring the iron solution into the solution of ferrocyanide—"soluble" Prussian blue is formed. This substance is only soluble in pure water, so that it does not dissolve until the mother liquor has been removed and the blue washed. Formerly, soluble Prussian blue was much used for making inks, but it is now largely replaced by aniline dyes.

Turnbull's blue is a variety of Prussian blue prepared by the double decomposition of potassium ferricyanide with a ferrous salt. Its composition is said to be represented by the formula $Fe_3(FeCy_6)_2$.

Prussian blue is extremely fast to light and acids, but is decomposed and decolorised by the weakest alkalies, even by soap. It is soluble in oxalic acid, the solution being made use of in the preparation of blue inks, in place of one of soluble Prussian blue.

Smalt.—This pigment is now less used than formerly, as it has been largely replaced by ultramarine. It consists of a potash glass containing cobalt oxide instead of lime. Its composition is represented by the following analysis:—

	Per cent.
Silica,	70·86
Potash (and soda),	21·41
Cobalt oxide,	6·49
Alumina, iron, oxide, &c.,	1·24
	100·00

Smalts much richer in cobalt (up to 16 per cent.) are also prepared.

The raw materials consist of cobalt oxide, quartz and potassium carbonate. The first of these is obtained by roasting cobalt ores (see *Cobalt*, Vol. I., p. 197) to oxide (the crude oxide being termed **zaffre**), and is then mixed with a quantity of quartz, which is varied according to the required dilution of colour. To this mixture about one-third of its weight of potassium carbonate is added, together with an oxidant (usually white arsenic), to convert ferrous oxide into ferric oxide. The mixture is then charged into fire-clay crucibles, and heated to its fusing point, in a furnace resembling a glass furnace (Vol. II., p. 153). When the mass is fused, a "speise" or regulus (consisting of iron

and nickel sulphides and arsenides that have not been oxidised by the preliminary roasting, which is purposely limited, in order that sufficient arsenic and sulphur may remain for the formation of this speise) falls to the bottom of the crucible. When this separation is complete the glass is ladled out and the speise run off through holes in the bottom of the crucible, which are plugged during the fusion. The fused glass or smalt is thrown into cold water, and the resulting, roughly granulated mass is ground and levigated. Smalt is a very permanent pigment.

Artist's "**Cobalt Blue**" generally consists of cobalt oxide and alumina, and frequently contains cobalt phosphate. It is made by precipitating a mixture of alum and cobalt nitrate with sodium carbonate, and heating the precipitate to redness. An alternative plan consists in igniting cobalt phosphate with alumina.

There is a variety of blue pigments consisting of copper carbonate or hydroxide, or both—*e.g.*, **Bremen blue** and **blue verditer**. A copper-lime glass was anciently used, notably by the Egyptians, as a blue pigment. A sample analysed by Fouque contained 64 per cent. SiO_2, 14 per cent. CaO, 21 per cent. CuO, and a little ferric oxide.

3. **GREEN PIGMENTS.—Brunswick Green.**—The green pigment of chief commercial importance is that prepared by mixing a yellow pigment, lead chromate (*v.i.*), with Prussian blue (*v.s.*). This colour is "let down" by such diluents as barium sulphate, calcium sulphate, calcium carbonate, lead sulphate and white lead. The pigments may be incorporated dry, or precipitated together, in which case solutions of lead acetate, ferrous sulphate, potassium ferrocyanide and potassium bichromate are mixed, and the diluent—*e.g.*, barium sulphate—added, the mass being more evenly commingled than that prepared by the dry method. "Brunswick green" is the name most commonly applied to these pigments, although genuine Brunswick green (now practically obsolete) is an oxychloride of copper. The following analyses, by Hurst, show the composition of pigments of this class:—

	Pale.	Deep.
	Per cent.	Per cent.
Water, ...	1·000	1·000
Barium sulphate, . . .	72·744	72·764
Calcium sulphate, . . .	2·341	Trace
Prussian blue, ...	0·929	4·543
Lead chromate, . . .	14·266	17·660
Lead sulphate, . . .	8·073	3 280
	99·353	99·247

These greens are used as common green paints, but as they contain lead they darken in air containing sulphuretted hydrogen.

Chromium Greens.—Chromic oxide is the basis of several green pigments. Thus, **chrome green** consists essentially of Cr_2O_3, and is prepared by igniting mercurous chromate, ammonium chromate or a mixture of potassium chromate or bichromate and ammonium chloride, or one of potassium bichromate and sulphur. In the two latter cases the pigment has to be freed from soluble salts by washing. Hydrated chromic oxide is now generally prepared in the form known as **Guignet's green.** By Guignet's process, one part of potassium bichromate is mixed with three parts of boric acid, and heated to dull redness in a muffle. Chromium borate, $Cr_2(B_4O_7)_3$, is formed, and on treatment of the mass with water is split up into hydrated chromic oxide, $Cr_2O(OH)_4$, and boric acid. The temperature at which the ignition is effected lies between 500° and 700° C. = 932° to 1,292° F. Guignet's green is very permanent and is free from the hygienic disadvantages of arsenic greens, but is costly to prepare. Several other green pigments containing chromium—*e.g.*, those prepared by boiling an alkali phosphate with potassium bichromate and a reducing agent such as invert sugar, consisting mainly of chromium phosphate—are also manufactured.

Greens containing Copper.—The copper greens having the best colour are those which contain arsenic, viz.:—**Scheele's green** and **emerald** or **Schweinfurth green.** The former is an acid cupric arsenite, $CuHAsO_3$, and is made by dissolving arsenious oxide (As_4O_6) in a solution of potassium carbonate and pouring the solution into one of copper sulphate. The precipitate is of bright green colour, but is very objectionable on account of its tendency to form dust in the air, such dust being highly toxic. The latter (emerald green) is an aceto-arsenite of copper, $Cu(C_2H_3O_2)_2 + Cu_3As_2O_6$, and is generally prepared from verdigris, which is a basic acetate of copper (*v.i.*), by boiling it with arsenious oxide. An alternative plan consists in mixing solutions of copper sulphate and sodium arsenite, and treating the precipitate of cupric arsenite with acetic acid. The pigment is permanent but poisonous.

Verdigris is a basic acetate of copper, $Cu(C_2H_3O_2)_2 + Cu(OH)_2 + H_2O$, and is prepared by the corrosion of copper plates, by means of the acetic acid present in wine residues that have been allowed to acetify. Another process consists in laying plates of copper between sacking, saturated with pyroligneous acid (see *Distillation of Wood*, Vol. II., p. 92). These layers are packed in casks, the sacking being periodically withdrawn and again saturated with the acid. When the copper plates have become coated with verdigris they are scraped and replaced. A crystalline variety of the pigment, obtained by dissolving

copper oxide in pyroligneous acid, or by precipitating copper sulphate with calcium acetate, and evaporating the solution obtained in either case to the crystallising point, is known as "distilled verdigris."

Green basic copper carbonates—*e.g.*, **green malachite**, $CuCO_3.Cu(OH)_2$—are prepared by the levigation of the natural mineral, or by precipitating a solution of copper sulphate with sodium carbonate. In the latter form, the pigment is sometimes called "**green verditer.**"

Terre verte is a native mixture of silicates, ferrous silicate predominating. A sample from Cyprus was analysed by Klaproth, and had the following composition:—

	Per cent.
Silica,	51·5
Ferrous oxide,	20·5
Potash,	18·0
Magnesia,	1·5
Water,	8·0
	99·5

Rinmann's green is prepared by igniting either zinc oxide which has been saturated with the solution of a cobalt salt, or a mixture of the hydroxides of zinc and cobalt. It is a good permanent pigment, but is costly to manufacture.

4. **YELLOW PIGMENTS.—Chrome Yellow.**—The most important yellow pigment is chrome yellow (lead chromate), which varies in shade according to its degree of basicity, neutral lead chromate ($PbCrO_4$), being a normal yellow, while the various basic lead chromates range from yellow to red, through orange. Yellows which are paler than lead chromate are made by "letting down" the neutral salt with a diluent, such as lead sulphate or barium sulphate. Chrome yellow is prepared by precipitation, solutions of potassium bichromate and lead acetate or nitrate being mixed in the proportions represented by the equation (in the case of nitrate)—

$$2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2KNO_3 + 2HNO_3.$$

An alternative method consists in digesting lead sulphate—which is a bye-product in calico-printing from making aluminium acetate by the interaction of lead acetate with aluminium sulphate—with potassium bichromate, the lead chromate formed being in this instance mixed with lead sulphate. The same mixture is prepared according to the reaction represented by the equation given above, with the difference that sodium sulphate replaces a part of the potassium bichromate, the shade obtained depending upon the proportion of sulphate used. Many other recipes involving the same principles are adopted in the manufacture of chrome yellow.

The orange and red shades of lead chromate are made by

digesting the neutral salt with caustic soda or milk of lime. These bases being more powerful than lead oxide, remove a portion of the chromic acid as sodium or calcium chromate, the resulting colour depending upon the proportion of base used and upon the conditions of digestion. The following equation shows the formation of the red basic chromate, which, when associated with unaltered yellow neutral chromate, gives various shades of orange :—

$$2PbCrO_4 + Ca(OH)_2 = PbCrO_4.Pb(OH)_2 + CaCrO_4.$$

Chrome yellows are sold under various trade names, the paler yellows—*e.g.*, "**lemon yellow**"—being termed "pure," when the diluent used is lead sulphate instead of barium sulphate. Chrome yellow, as found in commerce, is but rarely pure chromate of lead, often containing up to 40 per cent. of diluents. The chrome yellows cover well, but are darkened by air containing sulphuretted hydrogen.

Zinc chromate and **barium chromate** are also used as yellow pigments to a limited extent.

Cadmium yellow is CdS, which exists in two shades, the yellow sulphide being precipitated when sulphuretted hydrogen is passed through a neutral or slightly acid solution of a cadmium salt, and the orange being formed when the solution is strongly acid. It is unaffected by sulphuretted hydrogen.

King's yellow is As_2S_3, and occurs naturally as **orpiment**, but is more frequently artificially prepared by precipitating a solution of white arsenic in hydrochloric acid with sulphuretted hydrogen, or by subliming a mixture of sulphur and white arsenic.

Another sulphide of arsenic—**realgar**, As_2S_2—used as a pigment, is red, and occurs native, though it is also prepared by heating white arsenic with a limited supply of sulphur, or with a mixture of charcoal and sulphur, the sulphide subliming.

Turner's or **Cassel yellow** is an oxychloride of lead ($3PbO.PbCl_2$), prepared in a manner similar to that used in the first stage of the manufacture of white lead by Milner's process (p. 351), the product, hydrated lead oxychloride, being fused ; the shade depends upon the duration of the heating.

Naples yellow is lead antimoniate, and is made by heating a compound of antimony—*e.g.*, tartar emetic with lead oxide.

Cobalt yellow ("*Aureolin*") is the double nitrite of potassium and cobalt, prepared by adding a solution of potassium nitrite to one of cobalt acetate.

Yellow ochre will be dealt with under *Brown Pigments.*

5. **RED PIGMENTS.—Red Lead** (*Minium*).—This oxide of lead is an oxidation product of litharge (PbO), and may be regarded as an association of PbO and PbO_2. The composition of commercial red lead does not correspond with the formula

Pb_3O_4—*i.e.*, $PbO.PbO_2$—which is usually quoted, but with that of an oxide containing more lead monoxide—*e.g.*, $3PbO.PbO_2$. It is extensively made, not only for use as a pigment, but as a cheap oxidant for glass making and other purposes. It is produced by roasting lead oxide, which must be specially prepared for the purpose by oxidising metallic lead in a reverberatory furnace to a temperature just above the melting point of lead, 335° C. = 635° F., but too low to fuse the resulting lead oxide, the yellow form of lead oxide (**massicot**) being thus produced. The massicot is raked or rabbled off the lead as it is formed, and is then ground and levigated to eliminate metallic lead, which it always contains. The purified massicot is heated in a muffle at a low red heat until a cooled sample is found to have acquired the right hue. This colouration is caused by absorption of oxygen.

Red lead has good covering power, but shares the objections to lead pigments which have been already mentioned. **Paris red**, or **orange red**, is made by cautiously heating white lead.

Vermilion.—This substance is mercuric sulphide (HgS), which occurs in two modifications, the black and the red. The preparation of red mercuric sulphide can be effected by both dry and wet methods. The dry method, which is said to produce the better quality, consists in heating mercury with sulphur, the quantities varying according to the prescription employed. In the Chinese process the first heating is conducted in an iron pan, whereby a dark coloured mass results. This is powdered and sublimed in a pan surmounted by a receiver constructed of porcelain tiles. The sublimed vermilion is ground, and mixed with water containing a little alum and glue. From this it settles and agglomerates, the deposit being cut into cakes for the market. Processes similar in principle are practised under the names of the Dutch and Idrian processes.

The wet method consists in heating an intimate mixture of 300 parts of mercury and 114 of sulphur with 75 parts of caustic potash and 400 of water at a temperature of 50° C. = 122° F., for some hours, the water lost by evaporation being made good during the earlier stages of the process. Towards the end of the operation, when the black modification of mercuric sulphide is changing into the red variety, the mass is kept stirred. This process depends upon the fact that black HgS is converted into red HgS when heated with alkaline polysulphides —in this case by potassium polysulphide formed by the action of sulphur on caustic potash.

Vermilion prepared by the expensive and empirical Chinese process is better in quality than that obtained by cheaper and more rational methods. Vermilion is often adulterated with red lead, ferric oxide, brick dust and pigments coloured with

eosin (vermilionettes—*v.i.*). It is permanent and non-poisonous. Its high specific gravity (8·2) renders it liable to separate from the vehicle with which it is ground.

Antimony vermilion, $2Sb_2S_3.Sb_2O_3$, is prepared by pouring a solution of antimonious oxide in hydrochloric acid into one of calcium thiosulphate (partially oxidised alkali waste), and heating at a temperature of about 60° C. = 140° F. The red oxysulphide is precipitated, and is washed and dried at a low temperature. It is a permanent pigment of good colour, but is not largely used.

Mercuric iodide, HgI_2 (brilliant scarlet), is prepared by precipitating a solution of mercuric chloride with one of potassium iodide, and is of great beauty, but is very fugitive.

6. **IRON PIGMENTS.**—The pigments containing ferric oxide as a colouring constituent are of various shades, usually less definite and brilliant than those already described, and therefore less conveniently classified in the order of their colours.

Red Oxide of Iron.—This is the commonest iron pigment and most closely approaches pure ferric oxide in composition. It is also known as **rouge**, and its various shades are known as **Indian red, Venetian red, &c.** Certain hæmatites of good colour are ground and used as a pigment, and ferric oxide prepared artificially is also largely employed. The principal source of the artificial variety is green vitriol (copperas). When this is ignited, as in the manufacture of Nordhausen sulphuric acid (p. 17, Vol. II.), it loses water, sulphur dioxide and sulphur trioxide, the residue being ferric oxide (**colcothar**). It is also prepared from the sulphates of iron produced by the oxidation of iron pyrites, as practised in this country where the pigment is the main product and the sulphur oxides are not condensed. Ferric oxide pigments can also be obtained by igniting the ochres (*v.i.*) this process allowing of the obtainment of a more extensive range of shades. Refuse liquors containing iron—*e.g.*, the pickling liquor from tin plate works (see Vol. I., p. 187)—are precipitated by lime, and the crude oxide of iron obtained, roasted and used as a pigment. The shade of ferric oxide depends on the temperature of ignition, a purple tone predominating in those specimens which have been most strongly heated. Red oxide pigments are extremely permanent and are largely used, chiefly for rough out-door work. They are commonly diluted with such substances as barium sulphate, calcium sulphate and calcium carbonate, and may contain from 50 to 95 per cent. of ferric oxide (*cf.* Vol. I., p. 44).

Ochres and Siennas.—As found in nature these differ from the red oxide pigments in that they contain hydrated ferric oxide, which is associated with clay and sand. In colour, ochres vary from yellow to brown according to the condition of the ferric oxide which they contain. Siennas are distinguished from

ochres by their containing manganese dioxide, and appear to have been deposited from suspension in water, for they are usually purer than ochres which may be regarded as formed by the decomposition of pyrites and other ferruginous minerals *in situ*. It thus happens that siennas can generally be used after simply grinding, whereas ochres require levigation. The best kinds of ochre are those from Oxfordshire and Derbyshire. The following is an analysis of Oxford ochre :—

	Per cent.
Water (hygroscopic),	6·89
„ (combined),	8·15
Ferric oxide,	12·81
Alumina,	6·47
Silica,	63·48
Lime,	1·00
	98·80

Ochres are permanent pigments; they are frequently adulterated with barium sulphate, calcium sulphate and calcium carbonate. Natural sienna is sold under the name of "**raw sienna**"; for the production of a reddish-brown pigment it is ignited until it has acquired the right shade, and is then known as "**burnt sienna**," the combined water of the hydrated ferric oxide being expelled by the ignition.

The umbers form another group of ferric oxide pigments, containing more manganese than the siennas, and, like the latter, are sold as **raw** and **burnt umber**.

B. **ORGANIC PIGMENTS.**—These may be divided into pigments containing free carbon and those owing their colour to complex organic dyestuffs. The former include :—

Lampblack (*vegetable black*).—This is made by the checked combustion of oily and fatty materials, and collection of the soot produced. The process, as generally carried out, consists in allowing creosote oil or similar cheap hydrocarbon to drip upon a hot tray, where it burns with a very smoky flame, a slight draught carrying the smoke through a number of narrow brick passages in which the black is deposited. That caught at the end of these chambers is the finest and best as a pigment. On account of its mode of preparation lampblack contains oil and tarry matter, but no mineral impurities or ash. It contains about 90 per cent. of carbon, the balance being tarry matter. For the manufacture of printing ink, lampblack is calcined to remove oily matter. A variety of lampblack of inferior covering power is called "**carbon**" or "**diamond**" **black**, and is the soot collected from the incomplete combustion of natural gas (see *Petroleum*, Vol. II., p. 118) by allowing the flame of the gas to impinge upon a revolving iron plate; it contains 92 to 93 per cent. C, 5 to 6 per cent. O, and 1 to 2 per cent. H.

Bone and Ivory Black.—Bone black is produced by the destructive distillation of bones (see Vol. II., p. 103). Scrap ivory is the raw material of genuine ivory black. In each case the colouring matter is carbon, which is diffused over the surface of calcium phosphate, that being present to the extent of about 75 per cent. of the weight of the pigment. The pot method (see *Destructive distillation*, Vol. II., p. 103) is generally used, as it yields a better pigment. Common black pigments consist of diluents, such as barium sulphate, coloured with about 10 per cent. of carbon.

Other Organic Colouring Matters.—In order to make use of colouring matters which, by reason of their solubility or poor covering power, are in themselves inapplicable as pigments, the plan of precipitating them upon a mineral "base," such as barium sulphate (**blanc fixe**), kaolin and alumina, is now largely adopted. A decoction of the dyestuff is made, and, if the colouring matter be "acid" in character, is precipitated by the addition of alum and stannous chloride, with or without sodium carbonate, in the presence of the diluent ("base") to be coloured. In the case of basic colours, their solutions are precipitated by the addition of tannic acid, and thus also colour the "base." The colouring matters used for the production of pigment lakes are considered under the head *Dyestuffs* (*q.v.*). The preparation of a few pigments, typical of this class, is given below.

Cochineal carmine is prepared from a decoction of cochineal by the addition of such precipitating agents as alum, stannous chloride and carbonate of soda, and allowing the carmine thus produced to settle. The following shows the composition of a good sample:—

	Per cent.
Water,	15·69
Ash,	7·24
Nitrogenous matter,	20·31
Colouring matter,	56·36

The ash consists chiefly of lime and alumina.

Magenta lake is made by precipitating the basic colouring matter **magenta** (*fuchsine*) with tartar emetic and tannic acid, in the presence of barium sulphate.

Vermilionettes are made from the acid coal-tar colour eosin (*q.v.*) by precipitating a solution of eosin in sodium carbonate with lead acetate in the presence of red lead or chromate of lead.

Sepia.—This is a brown pigment prepared by drying the peculiar secretion of the cuttle-fish (*Sepia officinalis*), and boiling it with caustic alkali, whereby it is dissolved away from accompanying impurities. It is a feeble organic acid, and can be precipitated from its solution in an alkali by an acid. The dried secretion contains 78 per cent. of the pigment, which has been

termed **melanin**, and some 17 per cent. of calcium and magnesium carbonates.

Indian yellow, or **purrée**, is made from the urine of cattle fed on mango leaves. It appears to consist of the magnesium salt of euxanthic acid ($C_{19}H_{16}O_{11}Mg,5H_2O$), which is insoluble in water, but not very stable, so that the pigment is liable to fade.

C. **PAINTS AND VEHICLES.**—In order to apply the pigments that have been described above, it is necessary that they should be used in a state of suspension in some liquid vehicle. In this condition they constitute **paints**. In those cases where paint is to be applied as a preservative it is essential that the vehicle should be capable of forming a coating or varnish-like film upon the surface, and thus attaching the pigment firmly thereto. For artists' use water is frequently employed as a vehicle, as no preservative effect on the surface painted is desired, but for industrial purposes a drying oil—*i.e.*, one which is capable of oxidising to a hard insoluble film—is requisite. A paint is said to be "ground in oil," or simply "ground," when it has been incorporated with a drying oil to a stiff paste, and to be "mixed" ready for use when the ground product has been diluted, to such a consistency that it flows readily from a brush, with a further quantity of a drying oil and a volatile solvent, such as oil of turpentine. For this reason pigments are met with in the market both "ground" and mixed, the former having to be mixed by the user.

The oil most commonly used is linseed oil, both raw and boiled (though other drying oils, such as walnut oil, are also employed), the paints being ground in raw oil and mixed with boiled oil. (For a description of linseed and other drying oils and an explanation of the terms "raw" and "boiled," see *Oils, Resins and Varnishes*, Vol. II., p. 233.) The dry pigment is generally reduced to powder by edge-runners. An edge-runner is a mill consisting of a rotating bed-plate on which bear a pair of vertical rollers, the pigment being ground between the plate and the rollers. It may then be **levigated**—that is, mixed with water to a cream; the coarse particles are thus separated, the finer flowing away suspended in the water, and being caught in depositing vats. The finely-divided colour is then ground in oil between millstones or rollers, the quantity of oil required varying, with the nature of the pigment, from 6 to 8 per cent. for white lead, 12 to 15 per cent. for ochre, and up to 50 per cent. for lampblack.

The mixing with boiled oil and oil of turpentine is effected in a **pugmill**, consisting of a vessel provided with an agitator driven by power. Instead of boiled linseed oil and oil of turpentine, more or less rosin oil and the lighter fractions of petroleum oil are frequently employed, the product being, however, inferior to paint made in a legitimate manner.

CHAPTER XVI.

MANUFACTURE OF LEATHER, GLUE AND SIZE.

I. **LEATHER.**—The softness and pliancy of skin, combined with its considerable strength, would admirably fit it for various purposes were it not for the facts that it rapidly putrefies when in its natural moist condition, and becomes horny and brittle when sufficiently desiccated to be more permanent. It is the object of the tanner and the leather dresser to render the skin imputrescible, and at the same time to preserve its pliancy and, in some cases, its softness. Diverse processes exist for accomplishing this end, but all are capable of classification under the three heads—(1) Tanning with infusion of bark or other vegetable material; (2) tanning with mineral salts; (3) tanning with oils. The word tanning is here used as synonymous with curing the skin, whatever the method adopted, though in the trade the word is almost exclusively applied to the first class of processes; skins which are treated by the processes belonging to the second and third classes are said to be "dressed."

RAW MATERIALS.—(1) **Hides and Skins.**—In order to appreciate what little is known as to the fundamental principle underlying the processes of tanning and leather dressing—namely, the relationship between the hide or skin and the tanning material (see *Theory of Tanning*)—some knowledge of the histological structure of the skin is essential.

This structure is practically identical in all skins, the tanner's differentiation of hide from skin referring simply to the thickness of the material and the kind of leather which it is to produce.

Fig. 42 represents a transverse section of a piece of calf skin, parallel to the plane in which the hair grows, and magnified to some 30 diameters. It will be seen that there are two distinct layers in this section, which has been stained in order to render this differentiation more apparent. The darkly-shaded portion on the hair side is known as the **epidermis**, and constitutes a small fraction of the thickness of the skin; the lighter and more considerable portion is distinguished as the **corium**, or true skin.

The epidermis is constituted of nucleal cells, the total number of which is fairly constant in the adult animal, since the outer cells dry up and are constantly removed by abrasion, their place

being taken by the living cells beneath; these are nourished by the albuminous liquid of the corium, and multiply in the usual manner. It appears that the epidermis is the parent of the hairs and glands. The former have their rise in an accumulation of cells, which subsequently grows down into the corium, forming the hair sheath, and in this the root of the hair develops and grows into the shape of a bulb as the hair pushes its way to the surface. The botryoidal **sebaceous glands**, to be seen gathered round the hair, discharge fat, as a lubricant, into the hair sheath, whilst the **sudoriferous** or **sweat glands** (shown in the Fig. as lightly shaded spaces about the hair roots) discharge the perspiration by ducts which open through the superficial epidermis. The muscles (**erector muscle**) which serve to erect the hair for protective purposes are situated close to the sebaceous glands.

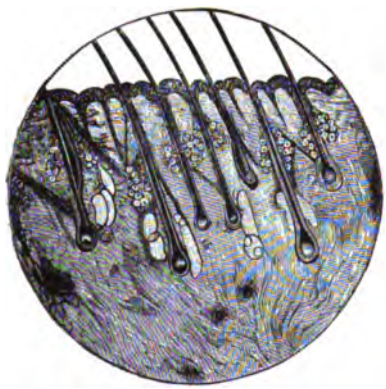


Fig. 42.—Section of hide.

Practically, the whole of the epidermis tissue is removed during the unhairing of the skin for tanning.

The **connective tissue**, which constitutes the corium, consists of bundles of fibres, which are loosely interwoven on the flesh side of the skin, but are more closely matted as they near the epidermis. The looser portion is termed the **pars reticularis**, and is the larger part of the corium; it is rich in fat cells, and is in great measure removed during the "fleshing" of the skin for tanning. The **pars papillaris**, as the portion of closer texture is called, is the most valuable part of the skin, its upper layer forming the **grain** of the leather. It has been stated that a membrane of different structure covers this pars papillaris, and separates it from the epidermis; the staining of this, the **hyaline layer**, by the colouring matter of the bark, may account for the difference which is to be noticed between the colour of the surface and that of the main portion of bark-tanned leather.

There can be no doubt that much advantage will accrue when the microscope becomes an accessory to every tannery; the information to be attained by the examination of sections of both successful and unsuccessful tannages, at all stages of the process of manufacture, will undoubtedly aid in the discovery of the cause of success or failure. Beyond the brief sketch of the structure of skin given above, it would obviously be foreign to

the scope of this work to enter into a discussion of the technique of microscope practice.

The chief proximate constituents of skin are either albuminoid compounds or closely allied to these; this is necessarily tantamount to saying that little is known of the chemical constitution of the histological units. The epidermis tissue consists mainly of **keratins**, which are characterised by their high content of sulphur, amounting in the case of hair to approximately 5 per cent., otherwise their composition does not differ much from that of the true skin given below. The keratins are much more resistant to the attack of water than is the true skin; when heated under pressure with water they yield a turbid solution, which is precipitated by acids with evolution of sulphuretted hydrogen. The solution does not gelatinise on cooling. When the skin is "limed"—that is, soaked in lime water, the less resistant, younger portion of the epidermis is attacked, so that the hair and superficial scales become loosened, and can be easily removed. Stronger alkalies and alkali sulphides apparently dissolve the hair.

The true skin, or corium, consists almost entirely (95 per cent.) of the compound called **collagen**; this is insoluble in cold water, but is converted into gelatine when boiled with water, a change upon which the glue-makers' art depends. This conversion is probably due to the combination of the collagen with water; it has been well compared with the change involved in the gelatinisation of starch. Both collagen and starch are bodies having a definite structure, which is entirely lost, without any apparent change in chemical composition, when they are boiled with water. The ultimate composition of gelatine (and of collagen) may be given as C = 49·91 per cent., H = 6·35 per cent., O = 25·52 per cent., N = 17·72 per cent., S = 0·50 per cent. Dilute mineral acids cause collagen to swell considerably; more concentrated acids dissolve it. Prolonged contact with dilute acids will convert collagen into gelatine even at the ordinary temperature. Alkalies dissolve collagen, but the action of lime-water in this respect is comparatively slow. In a bath of this alkali, the first action appears to consist in the dissolution of sufficient of the collagen to bring about the separation of the fibres of the connective tissue into still finer fibres. The addition of an acid to the solution precipitates a substance which has been termed **coriin**, though its right to be regarded as an individual is doubtful; it is soluble in a 10 per cent. solution of sodium chloride, and was at one time regarded as a cement substance—the "intercellular substance"—serving to keep the fibres together; in this sense it was said to bear the same relationship to the collagen as sericin bears to silk fibroin (p. 259); it is more probably only a decomposition product of the collagen. There are always several amido-acids and much ammonia to be found in lime-water which has been used for the unhairing of hides.

Gelatine will receive further notice under glue, but attention must here be called to two of its properties which are most significant for the tanner. One is that a solution of gelatine is precipitated by all true tannins, even when containing only 1 part in 5,000 parts of water. The other is the property which gelatine has of becoming insoluble when mixed with a solution of potassium bichromate and exposed to light. It is worthy of remark that gelatine is rendered insoluble by a solution of formaldehyde, HCHO (sold in the form of about 40 per cent. solution, under the name of formaline).

There is a certain amount of albumin, in the form of lymph, in the corium; it is for the most part removed during the preparation of the skin for tanning; what remains probably absorbs tannin. In addition to this there is another albuminoid substance, constituting the elastic fibres of the connective tissue; this is termed elastin, and is characterised by its great resistance to acids and alkalies, so that it is the last constituent to disappear when the hide is treated with these agents.

All the above constituents of the corium may be included under the term "true hide substance." Besides these, water, fat and ash are to be found in all skins. Since, in almost every case, the skin undergoes a process of unhairing, designed to remove the epidermis before tanning, it is better to consider the proximate composition of the prepared pelt rather than that of the raw hide. In the following table (*v. Schroeder*) the composition of a number of prepared hides is given:—

	Water.	In Anhydrous Hide.		
		Fat.	Ash.	Hide substance.
Sweated ox hide, . .	71·16	0·28	0·30	99·41
Limed „ „ . .	75·41	0·33	1·37	98·30
Calf skin, . . .	80·80	1·02	1·09	97·89
African kip, . . .	77·45	1·01	0·78	98·21
Cow hide, . . .	80·98	0·66	1·97	97·37
Sheep skin, . . .	88·59	6·98	1·19	91·85
Goat skin, . . .	81·55	2·58	0·45	96·67

The content of water in the prepared hide varies, both with the nature of the skin and with the preliminary process. Many skins are more spongy than others, and the texture of the same skin will vary in different parts; thus, the butt of an ox hide will contain 7 per cent. less water than the belly contains. When the skin has been limed it has been rendered more spongy ("plump") in texture, and, therefore, retains more of the water which it has absorbed from the limes and washing pits,

than does the sweated skin which has not plumped. That a limed hide should contain more ash than a sweated one is self-evident.

There appears to be a distinct difference, although a slight one, in the ultimate composition of the true hide substance of different classes of skins, as seen from the following figures:—

Class of Skin.	C	H	O	N	S
Ox, East India kip, horse, calf, cow,	50·51	6·43	24·98	17·88	0·20
Goat, deer, roe, . .	50·31	6·35	25·66	17·47	0·21
Sheep, . . .	50·19	6·49	26·06	17·05	0·21

The commercial classification of skins is into hides, kips and skins.

Hides are from the larger animals, the term having reference to the weight and thickness of the skin rather than to the animal from which it is derived. Oxen, cows and horses furnish the most important hides.

Skins are from calves, sheep, goats and the smaller animals generally.

Kips are from Indian and African breeds of small cattle, and are intermediate in size and weight between cow hides and calf skins.

Hides are tanned principally for sole, belt and harness leather (**heavy leather**). Calf skins are the principal raw material for the uppers of boots (**light leather**) and bookbinding; sheep skins furnish a variety of cheap leathers, such as imitation morocco, bazils, &c., and are especially useful for oil tannages, such as washleather; goat skins are *par excellence* morocco skins and glove skins, although lamb skins and deer skins furnish a good substitute in glove making. The rarer skins, such as dog, alligator, porpoise, &c., do not form staple raw material, although leather made from them is fashioned into fancy goods. As might be expected, the heaviest hides are from the cattle of the less cultivated countries, since artificial protection of the animal tends to render its skin thinner. The River Plate district is now the chief source of heavy hides for "butts." Young hides are generally more flexible and of finer fibre than old ones; the hides of cows which have calved become somewhat distended and thin. The practice of castration has considerable effect on the hide; thus a bull skin will be thinner in the back and thicker in the neck and belly than an ox hide, the castrated animal bearing a skin of more uniform thickness, and therefore better. Hides from diseased animals are nearly always inferior and, moreover, dangerous; in view of the frequent occurrence of anthrax among those who handle hides, a liberal use of anti-

septics, such as a solution of carbolic acid, in the tannery store room is to be recommended.

Similar remarks apply to the lighter skins, so that the sheep most prized for its wool will not yield the best skin. Practically nothing is known concerning the relationship between cattle-feeding and the quality of the hide. The chief defects in hides are cuts due to careless flaying, marks caused by adhering dung, marks of the branding iron, and thin places (even holes) due to the warble or bot fly. Protection against the last-named is to be obtained by painting places inaccessible to the animal with a mixture of flowers of sulphur and tar.

Imported hides have to be preserved from damage by putrefaction during transit. A common practice is to sprinkle salt on the flesh side of the "green" or raw hide. Mere drying by exposure to air will serve, but excessive sun's heat must be avoided, lest the skin be so altered that it gelatinise on being subsequently soaked in order to soften it. "Drysalting" is safer, and consists in drying the "green-salted" hide by exposure to air. East India kips are generally drysalted, and not unfrequently plastered with lime to make them heavier. "Arsenic kips" have been cured by white arsenic, and are usually yellow, being probably coloured with turmeric (for in the experience of one of the authors they turn red in the alkaline soaks); they take longer to soften in the soaks than do salt-cured kips. The use of naphthalene for preventing attack of insects when the skin is nearly dried, is practised.

(2) **Water.**—The character of his water supply affects the tanner both generally as a manufacturer and particularly as a tanner. The character of water from a manufacturer's point of view has been dealt with in the first section of this book (Vol. I., p. 98).

Water for the tanner should be free from suspended matter, for this is generally clayey material, containing sufficient iron to cause stains on the leather. For the same reason dissolved iron in the water is objectionable; as already explained, such dissolved iron is deposited when the water is allowed to stand or if it is softened by Clark's process (see Vol. I., p. 110).

The effect of hard waters on the production of leather is mainly connected with the "plumping" of the hide or skin and the consequent firmness of the leather. During the processes which are adopted for preparing the heavy hide for tanning, it is desirable that the fibres of the corium should be swollen, or "plumped," in order that a larger surface may be exposed for the absorption of tannin, and a firmer, more resistant leather be obtained than would otherwise be the case. For light skins, on the other hand, which are to be made into supple leather capable of being stretched, this plumping is less desirable.

It is found that in distilled water the hide is not perceptibly swollen. Water containing carbonic acid or carbonates of lime

and magnesia plumps the hide well, but water containing sulphate of lime or of magnesia has a still better effect. Water containing chlorides, however, is quite inimical to plumping. Thus the nature of the lime and magnesia salts which cause the hardness must be taken into consideration. In the light leather industry, where plumping is not desired, a water containing chlorides in reasonable quantity may even be advantageous; the effect of these salts in causing the skin to "fall" is no doubt connected with the solubility of coriin in saline solutions (p. 369).

Where hides are limed, in order to unhair them, as is generally practised in this country, the plumping effect of the water used for washing and soaking is of smaller importance, since the requisite plumping will be attained during the liming process. After the treatment in "the limes," the hides must be washed to free them as far as possible from the lime which remains in them; if a temporarily hard water (see Vol. I., p. 100) be used for this purpose, the carbon dioxide which it contains will tend to fix the lime in the form of carbonate, thus rendering the grain of the hide harsh, and causing the roughening of the surface during subsequent "scudding" operations; the staining of the leather in the tan pits, owing to such local depositions of calcium carbonate, is also liable to occur. Moreover, should the whole of the lime left in the hide be thus carbonated, the hide will fall. A soft or softened water is certainly desirable for this washing; the application of Clark's process (see Vol. I., p. 109) is to be preferred to the crude method generally adopted—namely, the stirring of a few pailfuls of milk of lime into the washing pit.

For the successful management of the "soaks," in which the hides and skins are washed and softened preparatory to unhairing, an equable temperature of the water is desirable in order that the process may not be at one time more rapid than at another, owing to the increased activity of micro-organisms induced by a rise of temperature. Well water, which has an average and constant temperature between 40° and 50° F. (= 4° to 10° C.), is preferable to river water, which is continually varying in temperature. It is necessary, also, to use with great caution any water which is contaminated with organic matter. If this be of vegetable origin it will be feebly acid, and will cause the hides to fall when they are washed in it after liming; if the organic matter be of animal origin the water will be far too good a breeding ground for putrefactive organisms.

There is a further objection to a very hard water in a tannery, namely, that it hinders the proper extraction of tanning materials, since all the tannins give insoluble compounds with lime and magnesia salts. The waste of tannins thus engendered is by no means negligible.

(3) **Tanstuffs.**—The term tanstuff may be conveniently applied to any material which may be employed for converting

skin into leather. Used in this broad sense the term includes (1) tanstuffs containing tannin, (2) oils, (3) mineral tanning materials. The special features of the oils and mineral salts which are used in tanning are considered in the appropriate sections of this work; it is here only necessary to deal with the tanstuffs containing tannin.

These materials are either parts of plants, or extracts made from parts of plants. They all contain one or more tannins, but in addition various other soluble substances which have a considerable influence on the tanning process.

The word **tannin** is applied to a number of chemical individual substances, composed of carbon, hydrogen and oxygen. Pending a more perfect means of isolating the substances, and a more exact knowledge of their chemical constitution than we at present possess, they may be distinguished by the names of the tanning materials of which they are the characteristic constituents; thus, they may be spoken of as oak tannin, myrobalans tannin, valonia tannin and so on. Some writers refer to them all as tannic acids, and distinguish between gallotanic acid (from oak galls), quercitannic acid, sumactannic acid and so on; it were better, however, to reserve the name tannic acid for the typical tannin, of which the constitution is known, namely, the purified tannin from oak galls (gallotannic acid).

Tannic acid is digallic acid, $C_6H_2(OH)_3CO.O.C_6H_2(OH)_2COOH$, and occurs in the form of a glucoside in **gall nuts** or **oak galls**, constituting the tannin of these excrescences. There are several varieties of gall nuts, those which are most highly valued being the **Levant galls**, produced by the puncture of the insect *Cynips Gallae tinctoriæ*, on the twigs of *Quercus infectoria*, a small tree growing in Asia Minor; these contain 60 to 70 per cent. of tannin and 2 or 3 per cent. of gallic acid. Immature galls are dark coloured (black or blue galls), and contain more tannin than is present in those from which the insect has bored its way—by which time the gall will have become lighter in colour (white galls) and pierced by a hole which serves to identify the mature gall even though it be fraudulently dyed. **Chinese** and **Japanese galls**, from *Rhus semialata* and *Rhus Japonica*, are lighter in colour than the best Levant galls and more irregular in shape. They contain 69 per cent. of tannic acid and 4 per cent. of other tannins. **Knoppern** or **acorn galls**, from *Quercus pedunculata*, contain 40 to 50 per cent. of tannin. **Bassorah galls**, **rove**, and the galls from the English oak (*Quercus robur*) contain 20 to 30 per cent. of tannin.

The tannin of galls is extracted on a large scale, chiefly for use as a mordant, by crushing the galls, and systematically extracting them with water at 40 to 60° C. (= 104 to 140° F.) until a concentrated liquor is obtained; this is allowed to settle, filtered and agitated with one-quarter of its volume of commercial

ether (containing alcohol). When complete separation into two layers has occurred, the ethereal solution of the resins, colouring matters, gallic acid, and fat is drawn off for the recovery of the ether, whilst the aqueous layer, containing the tannin, is distilled to a syrup and then spread upon tin plates, which are heated by steam until the tannin swells up and becomes perfectly dry. If "crystal tannin" is to be manufactured, the syrup is run through a colander on to a revolving hot copper cylinder, whereby it is dried in the form of strings, and has a crystalline appearance when broken up. The extraction of tannin from galls is sometimes effected by dilute alcohol alone, or by water alone, the products being distinguished as **alcohol tannin** and **water tannin**; they are more impure than **ether tannin**.

Commercial tannic acid thus prepared, contains from 70 to 90 per cent. of digallic acid, the remainder consisting for the most part of glucose and water, and also, usually, some gallic acid. The glucose is present as still undecomposed tannin, most of the tannin having broken up during the extraction. Tannic acid is amorphous, and generally of a brownish tint; it has an astringent taste, and should dissolve completely in six parts of cold water, and in alcohol. When hydrolysed by being heated with acid or alkali, it yields **gallic acid**—

$$C_6H_2(OH)_3CO.O.C_6H_2(OH)_2COOH + H_2O = 2C_6H_2(OH)_3COOH$$

showing it to be an anhydride produced from two molecules of gallic acid (trihydroxybenzoic acid). Gallic acid is prepared for the manufacture of some dyes (see *Gallocyanin*) and of **pyrogallic acid** (pyrogallol, $C_6H_3(OH)_3$—a photographic developer), into which it is converted by elimination of CO_2, effected by heating under pressure with water.

When tannic acid is heated it yields a sublimate of pyrogallol. An aqueous solution gives a blue-black colour or precipitate with ammonium ferric sulphate, according to the strength of the solution. A tannic acid solution gives a precipitate in a solution of gelatine. When a piece of raw hide is immersed in the solution of tannic acid, the whole of this is absorbed, the hide becoming converted into a poor form of leather.*

The above properties of tannic acid are typical of all the tannins, the last two being most significant from the tanner's

* Wagner classified tannins into pathological and physiological tannins. The former class includes all tannins which are the result of morbid metabolic changes in the plant—*e.g.*, the tannin produced in the formation of nut galls, which result from injury to the plant. The physiological tannins are normal products of the metabolism of the plant, such as the tannin of oak bark. Since a marketable leather cannot be produced from the use of galls by themselves as a tanning material, it was formerly held that the physiological tannins could alone tan hide. It is now agreed, however, that this incapacity on the part of galls is due to the absence of other soluble constituents which occur in oak bark, and not to any specific property of oak tannin not possessed by gall tannin.

point of view. All tannins may be regarded, like tannic acid, as condensation products of two or more molecules of polyhydroxybenzoic acids, or as derivatives of such products, existing in the plants as unstable glucosides.

They do not all, however, yield pyrogallol when heated, nor a blue colour with ferric alum; in fact, in lieu of a better classification, it has become customary to divide the tannins under two heads:—(1) Those which yield pyrogallol when heated, and are therefore related to gallic acid; (2) those which yield pyrocatechol, $C_6H_4(OH)_2$, when heated, and are therefore related to protocatechuic acid, $C_6H_3(OH)_2.COOH$. It is also generally true that the tannins of the first of these classes (**pyrogallol tannins**) give a blue colour with ferric alum, whilst those of the second class (**pyrocatechol tannins**) yield a green colour with the same reagent. From the investigations of Trimble the further distinctions may be drawn that (1) the pyrogallol tannins contain, on the average, 52 per cent. of carbon and 3 per cent. of hydrogen, and give no precipitate with bromine water; and (2) the pyrocatechol tannins contain, on the average, 60 per cent. of carbon and 5 per cent. of hydrogen, and give a yellow precipitate with bromine water.

A practical distinction, known to the tanner, between the two classes of tannins, is that the tanstuffs containing the pyrogallol tannins yield a "bloom" on the leather, which is a whitish deposit of the so-called ellagic acid, $C_{14}H_6O_8$; whilst the tanstuffs containing the pyrocatechol tannins deposit a red colouring matter in and on the leather; this consists chemically of the substances known as phlobaphenes (**oak reds**), the constitution of which is not understood. Both ellagic acid and phlobaphenes can be obtained by heating the respective tannins with dilute acids, and they appear to partake of the character of anhydrides.

The tanner is only concerned with those constituents of the tanstuff which are soluble in water; these are very numerous, but may be classified as tannins, sugars, starch, gums, resins and a small quantity of soluble mineral matter. The tannins are, of course, the most important constituents of the material, but it has recently been shown that the other constituents, or at all events the sugars and starch, are by no means valueless in the tanning process. In the analysis of tanning materials it is not possible to differentiate one tannin from another; consequently the same material may, and probably does, contain more than one tannin, although in most either the pyrogallol or pyrocatechol tannins largely preponderate.

The commoner tanstuffs may here be mentioned.

Oak Bark.—In Europe the bark of *Quercus robur*, the common English oak, is most highly esteemed; the *Q. cerris* of Turkey and the chestnut oak (*Q. castanea*) of America are also prized for their bark. The bark is collected before it becomes corky,

which generally happens soon after the tree has reached the age of 15 years; May and June are said to be the best months for collection. The percentage of tannin in the dry bark varies from 10 to 16, decreasing with the age of the bark, and being higher in those trees which are grown on poor dry soil than in those grown in a damp and fertile country. This low content of tannin makes oak bark a very slow tanning material when it is used in the customary manner; the leather produced, however, is of the highest quality, though not of the greatest weight. The tannins of oak bark yield both blooms and reds.

Myrobalans.—This material is the fruit of *Terminalia chebula*, and is imported chiefly from India. The better, light coloured fruit consists of about 67 per cent. of rind and 33 per cent. of stone; the rind contains some 42 per cent. of tannin, whilst the stone contains 2·5 per cent., the average for the whole fruit being about 30 per cent. (on the air-dried material, containing 13 per cent. of moisture). It is not profitable to separate the stones, although they are hard to grind; the whole fruit may be profitably extracted by boiling water. The tannins in myrobalans appear to consist almost entirely of pyrogallol tannins, gallotannic acid being present; consequently the material blooms well. It gives a greenish-yellow colour to the leather and a porous tannage, so that it is not used alone, but may be advantageously employed with materials, such as hemlock, which yield a dark colour; it is much used with oak bark, and valonia.

Valonia, as imported into this country, consists of the cups of the acorns from *Quercus ægylops*, which grows in the Levant. The cups are covered with a "beard" (trillo) which is much richer in tannin than is the cup itself, and frequently becomes separated during the handling of the sample. The acorns are comparatively poor in tannin, and are not usually mixed with the valonia. Air-dried valonia (14·5 per cent. moisture) will contain about 30 per cent. of tannin; the beard contains about 45 per cent., the cups about 24 per cent., and the acorns about 15 per cent. Valonia contains both pyrogallol and pyrocatechol tannins, yields more bloom than does oak bark and gives a darker and heavier but harder leather; it is generally used with oak bark.

Sumach consists of the ground leaves of *Rhus coriaria* and is imported from the south of Europe. It contains when air dried (12 per cent. moisture) from 16 to 30 per cent. of tannin, which is almost entirely gallotannic acid. Sumach is unsuited for heavy leather tanning, but may be used with other materials as a corrective of colour; its chief application is for tanning sheep and goat skins.

Gambier or **Terra Japonica** is an extract prepared from the leaves and young shoots of *Uncaria gambier*, and is imported chiefly from Singapore. It is very similar to **cutch** or **catechu**,

an extract from *Acacia catechu*, which, however, is used mainly by the dyer (p. 326). Gambier occurs in the market both as "block gambier" and "cube gambier"; the latter is the better. The one-inch cubes contain about 40 per cent. of tannin, and should show crystals of pyrocatechol when broken. Gambier tans very rapidly, but produces a very spongy leather; in conjunction with other materials it furnishes a good kip tannage.

Divi-divi is the seed pods of *Cæsalpinia coriaria*. When air dried (13·5 per cent. of moisture) it contains 30 to 50 per cent. of tannin. It would be one of the best heavy-leather tanning agents, were it not liable to fermentation and consequent damage of the goods.

Hemlock bark is from *Abies canadensis* and is the principal tanning material of the United States, where the tree is indigenous. It comes into this country chiefly as an extract. The air-dried bark (14·5 per cent. moisture) contains about 12 per cent. of tannin, of which about half is soluble in cold water. The tannin gives a very large proportion of "reds" so that the leather is heavy, but of too red a colour to suit the trade in this country.

Mimosa, or **wattle bark**, is from various *Mimoseæ*, or acacias, indigenous in Australia, where the bark is the staple tanning material. The air-dried bark (14·5 per cent. moisture) contains 20 to 40 per cent. pyrocatechol tannins; it yields a heavy and firm, but dark leather. In small proportion, however, it corrects the colour given by valonia.

Quebracho is from several hardwood South American trees. In its air-dry condition (14·5 per cent. moisture) it yields 15 to 25 per cent. of tannins, which have a bright red colour. It is chiefly used for making extracts.

Algarobilla consists of the fruit of *Cæsalpinia brevifolia*, and contains, when air-dried (13·5 per cent. moisture), up to 52 per cent. of tannins, resembling those of myrobalans.

Canaigre may be mentioned as a new tanstuff, from the introduction of which much has been promised. It is the "root" of *Rumex hymenosepalum*, a wild plant of New Mexico and Arizona, and contains about 15 per cent. of mosture and 20 to 40 per cent. of tannins, which impart a bright yellowish-orange colour to the leather, and belong to the pyrocatechol class. Canaigre is said to form a soft, strong leather, and to be valuable as a corrective of colour when used in conjunction with other materials. It may replace gambier.

The organic substances which can be extracted from a tanstuff by water, are conveniently classified into tannins and non-tannins. The proportion of either, and of each to the other, which is extracted, depends on the duration, and, to some extent, on the method of extraction. Thus, it has been shown that nearly all the tannins can be extracted by a few hours' digestion

with water, and that a prolonged treatment deteriorates the liquor by rendering more of the non-tannins soluble than would otherwise be attacked; it has also been shown that the proportion of water used has but little effect on the proportion of non-tannins extracted, a fact which indicates that prolonged digestion brings about the hydrolysis and, *pari passu*, the dissolution of matters which would otherwise remain undissolved. It must be remarked, however, that a certain proportion of non-tannin is desirable, indeed essential, in a tan liquor, if good leather is to be produced. The reason of this appears to be, that the presence of organic acids in the tanpit is conducive to the formation of a full and solid leather, and that such acids, generally lactic and acetic, are generated by the fermentation of sugars, or allied compounds, in the liquors. If this favourable influence of acids be admitted, the percentage of substances in the tanstuff which are convertible into acids must be of importance. The following table shows the average ratio of acid-yielding substances (compounds capable of reducing Fehling solution *) to tannin, present in the materials quoted in the above list:—

	In Air-dried Material.		
	Mean Content of Tannin.	Mean Content of Acid-yielding Substances.	Ratio of Acid-yielding Substance to 100 Tannin.
	Per cent.	Per cent.	
Oak bark (young), . .	10·10	2·65	26·2
Myrobalans, . . .	30·00	5·35	17·8
Valonia, ...	28·80	2·69	9·3
Sumach, ...	28·00	4·53	16·2
Gambier, ...	47·18	1·85	3·9
Divi-divi, ...	41·50	8·39	20·2
Hemlock bark, . . .	12·32	0·71	5·7
Mimosa bark, . . .	32·00	0·91	2·8
Quebracho wood, . .	22·00	0·25	1·1
Algarobilla, . . .	43·00	8·23	19·1
Canaigre, ...	30·00	6·24	20·8

It seems that those tanstuffs which serve for the production of full leather contain the highest ratio of acid-yielding substances to 100 of tannin.

It is stated by Villon that for the production of a good yield of soft heavy leather the hide should absorb from the liquor both tannin and non-tannin, and that that leather is the best which absorbs non-tannin and tannin in the ratio of 15 – 20 : 100, a result most easily effected when this ratio between these sub-

* An alkaline solution of cupric tartrate.

stances also obtains in the tanning liquor. The same chemist draws a distinction between assimilable non-tannins and those which are not assimilable, but resinoid in character; the smaller the proportion of the latter the better, and the inferior quality of many extracts is referable to the fact that this proportion is increased by the action of hot water, and by subsequent evaporation.

The preparation of a tanning liquor is generally accomplished in the tan-yard; the manufacture of "extracts" at a factory devoted to the purpose has extended of late, but these are used mainly as a supplement to the liquor made in the yard. For the successful extraction of a tanstuff this must be finely shredded, and the leaching must be systematic. The ground material is generally extracted in sunken pits (**leaches, latches, taps**) with false bottoms, and capable of holding some 50 cwts., the fresh bark meeting the most concentrated liquor; the water usually flows from the bottom of one tap to the top of the next. Extraction with hot water is not very general, though, if it were more widely adopted less tannin would be burnt with the spent tan than is now the case: it is necessary to remark, however, that the temperature best suited for the material to be exhausted should be first ascertained, for a temperature suitable for one bark may cause the conversion of tannin into insoluble anhydrides in another. Moreover, the observations made above must be borne in mind. Gambier is best extracted cold, whilst for mimosa hot water is absolutely necessary.

Spent tan is generally used for steam raising in the tannery. For firing ordinary boilers it is passed between rollers to express most of the water, but in deep grates (equivalent in action to producers) it may be burnt whilst wet, with the aid of a little coal. Treppenrost grates (*step grates*, Vol. I., p. 55) are also used.

Extracts are generally made with water near the boiling point; it is, however, desirable that the temperature should be as low as possible, compatible with complete exhaustion, and the exclusion of air from the extractor is advisable. Subsequent concentration to a syrup or solid should be conducted in vacuum pans (p. 171). Since many of the materials which are cheap enough for the manufacture of extracts part with a large amount of colouring matter to water, means have been devised to decolorise the extracts of these materials to render them capable of yielding a lighter coloured leather. The addition of a little blood, and then raising the temperature of the liquor, whereby tannin albuminate is precipitated, carrying down the colouring matter, is practised. This method, in common with others, has the objection that it causes a loss of tannin. In dissolving extracts for use as tanning liquors, it is necessary to use water at approximately the same temperature as that at which the original extraction was effected.

The following table illustrates the composition of the chief extracts in common use, but the various brands differ greatly in content of water :—

	Water.	Tannin.	Non-tannin Extract.	Ash.	Insoluble Matter.	Sugar.
Chestnut wood extract, . .	60·73	26·49	10·43	0·27	2·08	2·61
Hemlock bark ,, . .	50·60	31·00	...	...	...	4·42
Oakwood ,, . .	59·60	26·52	11·72	1·52	0·64	2·99
Quebracho wood ,, (solid)	16·72	73·99	6·67	1·17	1·45	1·04
,, ,, (syrup)	46·06	45·90	5·06	0·70	2·23	0·90

Extracts are not unfrequently adulterated with molasses. In dealing with both liquor and extracts their liability to fermentation and oxidation must be borne in mind.

With regard to the mineral salts and the oils used in tanning it will suffice to say here that for mineral tannage, alum, salt, bichromate, copperas, and a few other chromium and iron salts are used, whilst for oil tannage oils belonging to the fish-oil group, especially cod and whale oils, are applied.

PREPARATORY PROCESSES.—Before the hide or skin is tanned it is always submitted to certain preliminary treatment, having for its object the production of a pelt which shall be clean, free from hair, soft and supple in the case of skins for light leather, and well distended in the case of hides for heavy leather.

(1) **Cleansing and Softening.**—Market hides and skins—that is, such as have been sold to the tanner within a few hours of their removal from the animal—only require washing, to remove blood and dirt, before they are unhaired. Since no kind of water can be said to be free from a solvent action on hide fibre, it is obvious that a prolongation of the washing will result in loss of weight to the hide. In the case of salted goods the washing must be more thorough, to ensure the removal of salt, for the presence of this substance in the pelt will not only delay the unhairing process and prevent the proper "plumping" of the hide, but will give rise to the species of efflorescence known as "spueing" and to damaged grain in the finished leather.

Inasmuch as salt has a very considerable solvent action on hide fibre (p. 369), that which is washed from the salted goods should not be allowed to accumulate in the washing pit. Actual **soaking** of the hide for the purpose of bringing it back to its natural, soft condition is only necessary in the case of dried hides. The rapidity with which the **soaks** will effect this object depends on (1) the temperature at which the hide was dried, (2) the temperature of the soak, and (3) the age of the soak. Goods dried at an English summer temperature will sufficiently soften in a

few days, whereas heavy South American dried hides may take two or three weeks. That the temperature of the soak should have an influence on the duration of the process is obvious when it is remembered that the softening action is a solvent one; uniformity of temperature in the soaks is much to be recommended, deep well water being in this respect preferable to river water. The age of the soak and its temperature will determine the extent to which putrefaction of the dissolved hide substance will progress, and *pari passu* the alkalinity (due to ammonia and amines) of the water. It is found that soaks which are swarming with micro-organisms will soften hides very rapidly, but the danger that the micro-organisms will attack the hide substance too vigorously renders such putrid soaks unsafe.

The formation of thin places in the hide—sometimes amounting to pinholes (so-called "lime specks") in the thinner skins—damage to the grain (inducing it to "frizz" or roughen), and stains (caused by the development of pigmentary matters) are frequently due to the action of micro-organisms in the soaks; such injuries may to some extent be avoided, and the advantage of the rapidity induced by micro-organisms be retained, by constantly "handling" the hides—*i.e.*, drawing them from and replacing them in the pit—and thus preventing settlement of the organisms in patches on the hides. The introduction of antiseptics to prevent excessive putrefaction in soaks is practised; that most generally used is salt, which, however, has the objections already indicated.

To complete the softening of dried hides they must, when soft enough to be bent without cracking, be submitted to the "breaking" action of a machine called the "stocks." This consists of two mallets which are alternately raised by cams and allowed to fall on to the hides in a wooden box.

(2) **Unhairing.**—It was stated on p. 367 that the hair is an appendage of the epidermis; in order that it may be removed the epidermis must be thoroughly softened, whereupon it is possible to scrape the hair, and with it the rest of the epidermis tissue, from the hide. Almost any alkaline substance will effect the necessary softening, but that almost universally used in this country is lime. In America and on the Continent it is customary to submit the skins to a process known as sweating, which consists in exposing them to conditions favourable to incipient putrefaction, whereby the epidermis is loosened, the action being aided by the alkalinity of the ammonia produced during the process. Other depilatories are used, but generally only as aids to lime.

Liming not only effects the loosening of the epidermis, but converts the fat of the hide into a lime soap, which is more easily removed by subsequently scraping the hide, than the grease itself would be. At the same time, the solvent action of the lime on the hide produces a separation of the fibres, which

makes the pelt thicker, and is advantageous in the manufacture of heavy leather, owing to the fact that hide plumped in this manner will take up a larger percentage of tannin, and produce a heavier and firmer leather. When the hide is sweated, it has to be plumped either by lime or a dilute acid (which is equally effective) after the removal of the hair. For light leather plumping is not desirable, since suppleness is the great *desideratum*; but liming is none the less a useful method of unhairing light skins, for the sake of the removal of grease. It is becoming customary now, however, to degrease with volatile solvents, in some such continuous apparatus as is used for extracting oils (see Vol. II., p. 230); the perfect neutrality of the solvent enables such a process to be used at almost any stage of the manufacture of the leather; thus the method is replacing the use of hydraulic pressure by which the grease was formerly expressed.

The process of liming is conducted in pits, each of which is generally large enough to hold a 50 hide *pack*. For light skins about ½ lb. of quicklime per skin, and for heavy hides from 2 to 4 lbs. per hide, are common proportions; but these amounts are probably wastefully in excess. The lime is best slaked before it is put into the pit. A number of pits, commonly three, is worked systematically, the fresh hides going into the nearly spent limes; the process lasts from 4 to 12 days, and the hides are frequently handled in order that the pit may be "plunged" to agitate its contents, and bring fresh lime into contact with the water (a cubic foot of water dissolves nearly 1¼ ozs. of lime). The solvent action of the lime on the hide speedily causes the liquor to become sufficiently rich in organic matter to form a nidus for bacteria, so that old limes are apt to be putrid, and on that account dangerous, as liable to cause the leather to be thin; much ammonia is present in old limes. Warming the limes to about 90° F. = 32° C., is found to greatly expedite the unhairing process, but the plumping action of the lime is thereby much diminished. It is an American practice to use a very sharp (*i.e.*, new) lime for three or four hours, and then to transfer the skins to water at about 110° F. = 43° C., to complete the loosening of the hair.

Arsenic sulphide (*red or yellow arsenic; rusma*), As_2S_3, or As_2S_2, is frequently added to the limes to the extent of some 10 per cent. on the weight of the lime. The sulphur forms a sulphide (or sulpharsenite) with the lime, and this, like all soluble sulphides, is a rapid depilatory; it is claimed that the arsenious acid (calcium arsenite) acts specifically and as an antiseptic; the improving effect of white arsenic on skin has been asserted in other connections.

The use of **sodium sulphide** as a depilatory, particularly for light skins, is extending. It is generally employed in conjunction with lime; thus, a solution containing 4 to 5 lbs. of sodium

sulphide per gallon of water may be made into a paste with lime and spread on the hair side of the skin, which may then be folded and left for a few hours, by which time the hair can be brushed off, for the action of the sulphide is much more drastic than that of lime. Immersion in a solution of the sulphide, containing ½ to 1 lb. per hide, is also practised; it is very difficult, however, to wash out the sulphide completely.

Sheep skins are unhaired by being plastered with lime on the flesh side, and then placed, wool to wool, in heaps; after a short time it becomes possible to pull the wool from the skin.

Sweating is effected by suspending the hides or skins in a room—the sweating pit—which is either underground, or completely covered with earth to ensure a constant temperature of 60° to 70° F., = 15° to 21° C. The atmosphere in the room must be kept saturated with moisture, to which end steam must be admitted in winter, and in summer cold water must be sprayed in. In from three to seven days—during which time the hides have been repeatedly reversed, in order that the more rapid action in the upper, and, therefore, warmer part of the room, may affect all parts of the hides alike—the hair will be sufficiently loosened.

By whatever means the epidermis tissue and hair have been loosened, they are actually removed by scraping with a blunt knife. Hides for sole leather are then trimmed or "rounded," the portions which covered the belly, cheeks and shoulders of the animal being removed and tanned apart from the "butt," as the portion which covered the back and sides of the animal is called. The butt is the most valuable portion, since, on account of its greater thickness, it yields a heavier leather than does the "offal" (bellies, cheeks and shoulders). The trimmed hide is washed in water for a day, to remove the greater part of the lime which it still contains. It will be obvious that for this purpose water as free from chalk as possible should be used. The butts are now ready for the tanpits, except that they sometimes receive a scraping (**scudding**) on the grain side with a blunt knife, to remove any remaining epidermis and lime soaps.

(3) **Softening Processes.**—For leather that is to be soft and supple the plumpness produced during the liming process must be counteracted before the skin is tanned; it is customary, therefore, to submit all skins which are not destined for sole leather to some process capable of causing them to "fall"—that is, to become thoroughly soft. It was originally observed that the desired effect could be obtained by immersing the skins in some liquid which had become putrid, and thus the custom has arisen of using a liquid which is easily capable of undergoing a putrefactive fermentation. An infusion of dogs' dung or birds' dung fulfils this condition, and has long been used under the name of a "bate" or "puer," the process being termed "bating." Since such an infusion is always alkaline, it is not so well fitted for

the removal of lime as an acid liquor would be; hence, for the lightest leathers the treatment in the bate is followed by immersion in an infusion of bran, which is undergoing lactic fermentation; this process is known as the "bran drench."

The heavier of the light leather skins are generally bated with pigeons' dung, the bath containing about 1 peck of dung to 30 hides, and the process lasting for some three or four days, according to the prevailing temperature. This bate is reputed to be sharper in its action than the dog-dung bate, which is generally employed for lighter skins. With regard to the rationale of the bating process, what was said concerning the action of bacteria in putrid soaks will apply; there can be little doubt that the feeding of micro-organisms on the hide substance produces the beneficial effect. It must be remembered, however, that dung will contain unorganised ferments, such as trypsin and pepsin; it has been found that these will cause a skin to fall, even in presence of antiseptics, although the leather produced from such skins is not so good as that from bated skins. The action of soluble ammonium salts—which are always present in the bate—as solvents for lime must also be included among the influences of the process. Whatever the chemistry of the bate may be, the operation is objectionable both on account of its offensive character and of its uncertain action. This uncertainty is probably due to the dependence of microscopic life on temperature; it is well known that in warm weather, particularly when a sudden rise of temperature occurs, as in thundery weather, the action of the bate will become so much enhanced that the skins will be speedily riddled with holes. Constant agitation of the skins in a bate, to prevent local action, is essential; to promote rapid action the bates are sometimes warmed to 30° to 40° C. = 86° to 104° F.

Attempts have been made to substitute acids (for the most part feeble organic acids, such as naphthalenesulphonic acid, cresotinic acid, &c.) for the bate; these, however, can only act as lime solvents. It is claimed that glucose has been successfully used; if so, its effects are probably due to the fact that the commercial article can supply nutriment for bacterial life. A bath of dilute mineral acid (free from iron), followed by the bran drench, appears to be actually in use in some tanneries as a substitute for bating.

The bran drench is intended for the completion of the softening of such skins as have been imperfectly softened by the bate, and is more commonly used for the lightest skins. It consists of an infusion of bran in about 200 times its weight of water at 30° to 35° C. = 86° to 95° F. The starch of the bran is speedily converted into glucose and dextrin by an unorganised ferment in the bran, and the glucose undergoes a fermentation similar to, but not identical with, the lactic fermentation (see *Minor*

Chemical Manufactures, Vol. II., p. 417), and resulting in the production of lactic, formic, acetic and butyric acids. It is desirable that butyric acid fermentation should not take place, since the solvent action of this acid on the skin is considerable. The gases evolved (chiefly hydrogen) during the fermentation serve to distend the skins and render their contact with the liquid more perfect. The following figures (*J. T. Wood*) show the quantities of acid likely to be produced, in grams per litre:—Formic acid, 0·0306; acetic acid, 0·2402; butyric acid, 0·0134; lactic acid, 0·7907. An artificial mixture in these proportions has been found successful.

The time during which the skins are in the drench depends on the amount of previous bating which they have received.

TANNING PROCESSES.—(1) **Tanning with Tanstuffs.**—The varieties of vegetable-tanned leather are so numerous that a description of the system used for each cannot be here given, the more so as the chemical principles involved are the same for many. It will suffice to consider the systems in use for (*a*) leather for soles, (*b*) leather for dressing, (*c*) leather for dyeing.

(*a*) **Leather for Soles.**—For this kind of leather a process must be adopted which will produce the greatest possible solidity, combined with sufficient flexibility to prevent cracking. To the tanner it is advantageous that the maximum weight should be produced, and for the purchaser also, the weight per unit of area is a criterion of solidity. Hence the tannage for sole leather is conducted with materials which impart the maximum weight—by yielding certain proportions of other matters besides tannin to the hide—and in such a manner that the hide shall be tanned throughout. In order to effect this thorough tannage, it is essential that the hide should not be immersed in a liquor comparatively rich in tannin, until such time as it has become already slightly tanned, lest by the rapid tannage of the surface, the fibres should be so swollen that entry of tannin into the interior be hindered. It may be said that when once a partial tanning has occurred, the completion of the process will be the more rapid the richer the liquor (within limits) in tannin. When oak bark is the sole material employed as a source of tannin, the liquors can never be made strong enough by the method of leaching adopted (p. 380) to produce a rapid tannage. Consequently, until comparatively recently, when valonia, myrobalans, &c., were introduced, the tanning process was a very lengthy one, lasting even as long as two years. With regard to the use of tanstuffs which yield liquors rich in tannin, it must be remembered that, inasmuch as careless tanning with oak bark could originally be detected by the bad colour of the leather, the tanner is now somewhat hampered by the necessity for producing a leather which shall have a colour approaching that of good oak-bark tannage. In English practice, the butts

are first suspended in pits (**suspenders**) containing nearly spent liquors, which have served either in the handlers or **layers** (see below); they should be agitated by some mechanical rocker while completely immersed in the liquor. Several suspenders are generally used, and are worked systematically. The object of this process is, technically, to strike the colour of the leather, and, actually, to effect the partial tanning, to which reference has already been made; the attainment of this object depends very largely on the degree of acidity which the liquors possess. The function of the acid will be understood from the following considerations.

It is only possible to produce thick leather when the hide has been properly plumped—*i.e.*, so swollen that the entrance of the tannin can be effected easily. A hide may be either alkali-plumped or acid-plumped, the former being the case when it has been limed. As might be expected, the entrance of tannin, itself an acid-like compound, into an alkali-plumped hide is more rapid than into one which is acid-plumped. If there be no acid in the suspender, the hide being alkali-plumped, tannage will take place very rapidly; but owing to the tendency of combinations of lime with tannins to darken by oxidation, the colour of the leather produced will be bad. If there be sufficient acid to neutralise the lime left in the hide, but not more than this, the hide will fall, and plump leather will not be produced. A third possibility is that there should be enough acid in the liquor to dissolve all the lime from the hide, and to substitute an acid-plumped for an alkali-plumped condition; in this case the tannage will be slow—*i.e.*, the striking of the colour will take long—but this colour when produced will be good. For the production of the best leather, then, the acidity of the suspender liquors must be considerable, the more so as the hide tends to fall *pari passu* with the entrance of tannin, at all events during the early stages of tanning.

The acids present in these liquors are such as result from the fermentation of sundry of the soluble bark constituents in the earlier stages of the tanning. They are, of course, vegetable acids, acetic, butyric and lactic acids being the chief. Their amount is, to a certain extent, under control, since the materials most liable to fermentation (*e.g.*, myrobalans) may be used in the handlers.

In American and German practice hides for sole leather are sweated, so that they have to be plumped with acid before tannage. In America, plumping with dilute vitriol is practised; the Germans prefer to use a very acid liquor from the layers. It may be said that the German system of tanning is a "sour" one throughout, since even in the layers the liquor becomes highly acid owing to their degree of dilution and the dustiness of the material employed. A German suspender liquor, made

from sour bark, was found to contain, in grams per 100 c.c. :— Tannin, 0·226; non-tannin, 0·916; total acid (as acetic acid), 0·463; volatile acids (as acetic acid), 0·300; non-volatile acid (as acetic acid), 0·163; specific gravity, 1·0059 (5·9° barkometer).

From the suspenders the hides pass into the **handlers**; these are pits in which the hides are laid flat, in a heap, and from which they are "handled" every day. The series of handlers is worked systematically, the fresh liquor being run into the pit which is to receive the most fully tanned hides. It is advantageous to feed the hides in the handlers with rapidly tanning materials, such as gambier, hemlock extract, &c. After about a month has been spent in the handlers, the pack of hides is moved on to the first **layer**; here it is allowed to remain in strong liquor with a layer of tanstuff (bark, myrobalans, valonia) between each hide, the whole being covered with bark, to exclude air. The time of laying away varies considerably, from one to six weeks for each layer being quoted as usual. The thickest hides require twelve months for thorough tannage, but an average of eight to ten months is now common. Owing to the fact that the strength of liquors is judged solely by an erroneous criterion, the specific gravity (generally quoted in degrees of the barkometer—*i.e.*, the last two figures of the true specific gravity, water being taken as 1000 *), little is yet known as to the actual content of tannin requisite in the different layers. The last layer should contain the strongest obtainable liquor. In German practice a liquor containing more than 2 per cent. of tannin is seldom used. Up to 6 per cent. of tannin is common in English practice.

Systems designed to hasten the tanning of sole leather have been from time to time brought forward. They fall under the following heads:—(1) Keeping the hides in continual motion in the tanpit; (2) circulating the tanning liquor continuously around the hides; (3) forcing the liquor through the hides by pressure; (4) tanning with very strong extracts; (5) passing a current of electricity through the liquor in which the hides are kept in motion. The last of these has alone received attention from experts, and it appears to be established that by suspending hides on a rotating frame in a vat containing a strong (4·25 per cent. tannin) mimosa and gambier liquor, and using a current density of from 0·375 to 1 ampere per square foot of electrode (the electrodes being copper plates on the sides of the vat), at a voltage varying with the strength of the liquor, it is possible to produce the same quality of leather in one-sixteenth of the time taken to produce it when the hides are at rest, and in one-fourth of the time taken when the hides are in motion, but when no electric current is passed. Lack of substance ("hungry leather") generally characterises goods produced by such rapid processes.

* Thus, 15° barkometer indicates a liquor of specific gravity 1·015.

(*b*) **Leather for Dressing.**—This class of leather is destined for the uppers of boots, for saddlery, belts, and other purposes where a stout but flexible leather is required; it is generally **curried** or **dressed**, whence its name. The bated hides are frequently shaved with a sharp knife to reduce their thickness (**shaved hides**); sometimes this process is postponed until they have been partially tanned, when, however, the shavings are of no use as glue-pieces (see *Gelatine*, Vol. II., p. 396); sometimes thick hides are split, after partial tanning, by a knife consisting of an endless steel band which travels like a driving belt, and works against emery wheels to sharpen it. The tanning of dressing hides and of East India kips is carried out in a manner which is, to a certain extent, the converse of that employed for sole leather, since it is not desired to make a firm leather. Thus, the first treatment of the bated hides consists in handling them or "tumbling" them (in revolving casks) in a comparatively strong liquor devoid of acidity. The object of this "graining" process is to tan the grain of the hide rapidly, and to cause it to shrink into a number of wrinkles. The degree of the shrinkage will depend on the strength of the liquor. Gambier is frequently the material used for graining. The completion of the tannage is effected similarly to that of sole leather, if a bark tannage is employed, the liquor being somewhat weaker; but a much more rapid tannage is now obtained with valonia, mimosa, myrobalans and gambier, the liquors being sometimes heated. It is customary to tumble the leather in sumach as a concluding process, to correct the colour. The currying of the leather is treated of under *Finishing Processes*.

(*c*) **Leather for Dyeing.**—Such vegetable tanned leather as is dyed is commonly known as **morocco**. Genuine morocco is made from goat skins, but there is now a large trade in "roans" and "skivers." The former are sheep skins tanned whole, the latter are the grain sides of sheep skins which have been split for making wash leather and white leather. Both are tanned with sumach which leaves them pale enough for dyeing. When dyed they are called morocco. **Bazils** are dyed with bark. Goat skins are bated, drenched and tanned in sumach, at first in tubs, in which they are agitated with paddles, and then in handlers. Sheep skins for roans are sewed into the form of bags into which the sumach liquor is poured and through which it is allowed to drain, the operation being repeated two or three times. Skivers are merely paddled in sumach liquor. After drying for the dye-house, roans and skivers are said to be in the "crust" state.

(2) **Tanning with Mineral Salts.**—The only mineral salts which have as yet been employed for tanning are alum, chromium salts and ferric salts. It is noteworthy that these salts contain very feebly basic oxides, of the type R_2O_3; the deposition of these

oxides, in the form of basic salts, within the skin seems to constitute the tannage; the matter will receive further notice under *Theory of Tanning.*

(*a*) **Alum Tanning.**—Alum is never used alone, being always accompanied by salt. White leather, used for bottle coverings, &c., is made by tumbling sheep skin splits (*i.e.*, the flesh sides) with a liquor containing about 4 per cent. of a mixture of alum with $\frac{2}{5}$ of its weight of salt. The leather is wrung out, and slowly dried. Such leather readily becomes de-tanned in water.

In the tanning of kid, whether calf-kid or the true glove-kid, a process is adopted which may be regarded as a cross between alum tanning and oil tanning, and has received the distinctive name of tawing. In both cases particular care is taken to submit the skins to a thorough bating, drenching and scudding, since suppleness is very necessary, and, in the case of kid and lamb skins for gloves, the limes are always sharpened with arsenic, this being mixed with the lime before the latter has had time to cool after slaking. The tannage is effected by tumbling the skins in drums containing alum and salt, drying, and again tumbling in drums with a mixture of oil (generally olive), flour and egg-yolk. The last named mixture appears to fill the interfibrillar spaces of the skin, imparting the necessary softness and elasticity. A final stretching (staking) over a blunt knife fixed in a post, and, when necessary, shaving to reduce the thickness, finish the skins for the dye-house, unless a second "stuffing" with the egg-yolk mixture be deemed essential.

(*b*) **Chrome Tanning.**—This is effected by immersing the skins (goat or sheep), unhaired and bated as usual, in a solution of chromic acid (or bichromate of potash with hydrochloric acid), and subsequently passing them through a bath consisting of a solution of sodium hyposulphite or sulphite and hydrochloric acid. The skins absorb the chromic acid, which is subsequently reduced to a chromium salt in the sulphite bath; the chromium salt is probably decomposed by the fibre, chromic oxide remaining in the skin to the extent of some 4 to 6 per cent., calculated as $K_2Cr_2O_7$. Since chromic acid may have too corrosive an action on the hide fibre, it has been suggested to use a chromium chromate, prepared by dissolving chromic oxide in chromic acid. Chrome-tanned leather is used for glazed kid in the United States, for glove leathers, and as a substitute for calf-kid and chamois leather.

(*c*) **Iron Tanning.**—The use of ferric salts in conjunction with salt, as a substitute for alum and salt, has frequently been suggested. The best results are obtained by the use of basic salts, such as a ferric oxychloride, made by dissolving ferric hydroxide in ferric chloride. The patentee of one process suspends the hides from wooden frames and allows the ferric oxychloride and salt solution to flow down each side. Iron tanning is not yet practised to any extent.

(3) **Tanning with Oils.**—This consists in impregnating the skins with some easily oxidisable oil (most commonly cod oil or whale oil) and allowing them to heat, owing to oxidation of the oil, in heaps. In this way the skin is converted into an exceedingly soft leather, which readily absorbs water, but cannot be easily de-tanned by any agent. Such leathers are **wash leather** or **chamois leather**—the applications of which are well known—and **buffs**, used for soldiers' belting, &c.

For wash leather the flesh splits of sheep skins are used. They are very thoroughly limed, fleshed, washed and bated with a bran drench. They are then submitted to hydraulic pressure to remove water and grease, painted with cod oil and stocked (p. 382) for two or three hours. After this preliminary stocking, the skins are hung up in a warm drying room, again sprinkled with oil and stocked. This series of operations is repeated five or six times in order to replace completely the water in the skins by oil.

After the final stocking the leathers are thrown into bins, covered with sacking and allowed to heat, great care being necessary to prevent burning; during the heating much acrolein is evolved. Since only a portion of the oil has been utilised by the hide, a process is necessary for removing the remainder which renders the leather greasy. For this purpose the leather is submitted to hydraulic pressure, when a considerable quantity of semi-oxidised oil is expressed; this constitutes **dégras** (**moëllon**), valued as a currying agent. The remainder of the oil is removed by a bath of alkali, which is afterwards neutralised with sulphuric acid to recover the fatty acids; these constitute **sod-oil**, which is also used in currying, but is inferior to dégras for this purpose.

The leathers are finally stretched over a beam and scraped with a circular knife, having a central hole by way of a handle. Sun bleaching, or bleaching with sulphur dioxide, and stretching, complete the manufacture. Shammy (chamois) leather is said to be much improved if frozen while moist. Buffs are made in a very similar manner, from South American calf skins, which have been shaved on both grain and flesh sides, and bated.

It is stated above (p. 367) that the complete desiccation of a skin will preserve it from putrefaction, although the product will not be leather, since it will lack pliability. Much dried skin is, however, prepared for **parchment** and **vellum**. The former is made from the flesh splits of sheep skins. The skins are limed for two or three weeks, fleshed and split. The splits are again fleshed and are then tightly stretched in frames, scraped and washed with hot water. They are next painted over with a mud of chalk, which absorbs the remaining grease, again scraped and dried.

For vellum, Swedish calf skins are employed. They are soaked

in putrid soaks for a week, worked on the beam, limed for three or four weeks, unhaired, washed and fleshed. Skins from piebald animals will not serve for the best vellum, as they are particoloured. The prepared skins are stretched in frames and treated as described for parchment.

FINISHING PROCESSES.—No leather is fit for the market in the condition in which it leaves the tanhouse. In the case of sole leather the finishing process is chiefly designed to give the leather a presentable appearance, the drying of the goods, which must take place in any case, constituting the real difficulty in the finishing process. In the case of lighter leather, the final operations consist in stuffing the goods with grease, so as to impart the necessary softness to the leather.

(*a*) **Finishing Sole Leather.**—In order to improve the grain of the leather and at the same time to remove the bloom (p. 376), the butts are "struck out" (generally after they have been lightly oiled and left in a heap until a slight heating has occurred—a process known as **samming**) by means of a three-cornered knife, which is capable of stretching the grain without cutting it. A fluted or plain roller passed by power over the grain is now generally substituted for the striking-out pin. The drying of the leather must be gradual and must be effected in the dark; to these ends the drying shed is generally constructed with slats, which can be placed at such an angle as to exclude light, whilst admitting the maximum volume of air. Such sheds may be heated to about 70° F. = 21° C. in winter.

A good sole leather, when cut with a sharp knife, should show a section which is uniform in appearance and free from fleshy or horny streaks. When gradually bent, the grain should not break. It will absorb about 33 per cent. of water when soaked therein. If fully tanned it will have about the following composition:—

Water, ...	18·00
Fat and ash,*	1·30
Soluble tannin, ...	5·00
Soluble non-tannin,†	3·80
Pure leather substance,‡	71·90
	100·00

The percentage of hide substance is calculated from a nitrogen determination, on the basis that the true hide substance contains 17·8 per cent. of nitrogen. Leather is frequently adulterated with glucose, soluble salts and barytes.

Market hides should yield about 56 per cent. of their weight

* Containing CaO 0·30, SO_3 0·50. † Containing sugar 0·40.
‡ Containing hide substance 39·90, combined tannin 32·00.

of leather, green-salted hides about 75 per cent., and dry hides about 150 per cent.

(*b*) **Currying.**—Dressing leather is generally **scoured** by a machine which moves brushes and stones ("sleekers") over the leather. It is then **stuffed**, either by hand or in a tumbler, with tallow and oils. The oils preferred are such as readily emulsify with water, which may contain a little soap to improve the emulsion. Those generally used are castor, neatsfoot, cod-liver oil, whale oil, olive oil and sperm oil; the characteristic features of these have been dealt with in the section on oils (Vol. II., p. 223). Dégras (p. 391) is especially valued for currying, and owes its property, according to Eitner, to a nitrogenous substance—the dégras-former—which exists to a small extent in the cod oil used in chamoising, but to a greater extent in the dégras itself; this substance is insoluble in petroleum ether, and should amount to at least 12 per cent. in dégras containing 20 per cent. of water. Fahrion has denied the existence of a dégras-former, and attributes the peculiar properties of dégras to the presence of hydroxy fatty acids. The iodine absorption of genuine dégras should be very similar to that of its parent cod oil. Many imitations are on the market.

Russia leather is scented by dressing the flesh side with birch oil obtained by the destructive distillation of birch bark. Light leathers are generally blacked, if not dyed, by a mixture of lampblack and oil. Roans, skivers and kid are nearly always dyed. This is most commonly effected by means of dyewoods (p. 324), but synthetic colours are used to a considerable extent, particularly Bismarck brown.* Basic dyestuffs are readily fixed on the leather, since this is already mordanted with tannin; it is difficult, however, to keep the dye-baths clear, on account of the precipitation of the dye by such tannin as is removable from the leather by water. To remedy this, the leather should be first passed through a bath of tartar emetic to fix the tannin. In dyeing it is customary either to fold the skins grain outwards and immerse them in the dye-bath, or to brush the dye on to the leather as it lies on the table. To whiten leather it may be passed first through a bath of sugar of lead and then through dilute sulphuric acid, whereby lead sulphate will be precipitated in the leather. Artificial grain may be put on the leather either by folding it and rolling it under a board, or by mechanical rollers or stamps.

Japanned or enamelled leather (patent leather) is glazed by being stretched and coated with a varnish of linseed oil, ground with some pigment, commonly lampblack; this coat is dried by placing the leather, still stretched, in a stove at a temperature

* Most leathers are damaged by the high temperature necessary in alizarine dye-baths, but chrome-tanned leather is sufficiently resistant to be dyed with alizarine colours.

of 70° to 80° C. = 158° to 176° F., and another coat is applied, the operation being repeated until the desired thickness is obtained. A coating of a true black varnish imparts the final glaze.

Theory of Tanning.—In attempting to account for the retention of a tanstuff by hide fibre, difficulties are met with which recall those experienced in attempting to account for the retention of a dye by textile fibres (see p. 270), and just as there are those who support a "physical theory," and those who support a "chemical theory" of dyeing, so chemists have long been divided into two camps concerning the physical or chemical nature of the tanning process. There is, however, a further difficulty in the way of formulating a theory of tanning, engendered by the fact that the hide fibre is so far altered during the process that it is incapable of putrefaction, and, in the majority of cases, will not become gelatine when boiled with water.

Knapp is of the opinion that the tanning process is only due to the coating of the hide fibres with the tanstuff, be this a tannin, a basic salt or an oil. In accordance with this view, he defines leather as hide in which the individual fibres are prevented from adhering together when dry. The definition certainly finds support when a study is made of alumed leather, a product which can be closely imitated by merely dehydrating the skin by absolute alcohol; in neither case is the "leather" permanent, for boiling water will convert it completely into gelatine. In the case of leather made with tannin, however, the matter is different; well-tanned sole leather will yield no gelatine when heated with water, nor can more than an inconsiderable percentage of tannin be extracted from it by water, or even by caustic soda solution.

Attempts have been made to apply Witt's solid solution theory of dyeing (p. 271) to the tanning of hide, and the classical silk-magenta-alcohol experiment (*loc. cit.*) has been quoted in support of this theory. It must be remarked, however, that the solvent which will behave to bark-tanned leather in a manner parallel to that in which the alcohol behaves to the magenta-dyed silk, has yet to be found. It has been stated by v. Schroeder and Pässler that hide cannot absorb more than its own weight of tannin (calculated on the weight of the anhydrous hide), and it is supposed that this is a saturated solid solution of tannin in hide. According to former statements, upper leather is never completely tanned by bark, but depends for its complete conversion into leather on a species of oil tannage imparted during the currying process. The assertion of Stenhouse that upper leather yields 25 per cent. of its weight of gelatine when heated with water, supports this view; but v. Schroeder has given the following figures, which show that all properly tanned leather contains about the same proportion of tannin calculated on the content of pure hide substance in the hide :—

	100 Parts of Prepared Hide Contain		100 Parts of Prepared Hide give of Leather		
	Water.	Hide Substance.	Mean.	Poor Tannage.	Maximum Tannage.
	Per cent.	Per cent.			
Sole leather, . . .	71	29	64	55	75
Strap leather (cow hides),	75	25	57	49	67
Dressing leather (kips, horse hides), . .	78	22	50	43	59
Calf leather, . . .	81	19	41	35	48

The same chemist has shown that the amount of tannin which hide will absorb depends on the strength of the tanning liquor; this, he claims, could not be the case were the process a chemical one.

Tannin in 500 c.c.	Tannin Absorbed by 100 Parts of Anhydrous Hide.
Grams.	Grams.
1·74	33·50
2·61	48·10
4·35	68·60
8·71	77·90

It was found that if the hide were placed in a stronger liquor than the last-named, it became so rapidly tanned on the outside that the liquor never penetrated to the inside. By introducing the hide into successively stronger liquors, as in the tanning process, 100 per cent. of tannin was absorbed.

Reviewing the whole of the evidence above quoted, it must be admitted that Witt's solid solution theory will not apply to the tanning of leather with tannin, and that in this case the existence of a chemical compound of tannin with hide fibre must be conceded. In the case of mineral-tanned leather, where the whole of the tanstuff can be removed by water, Witt's theory may represent the true state of affairs. In oil tanning a similar dissolution of the oil in the fibre may occur, the oil subsequently becoming fixed by oxidation, much as indigo white is converted into indigo blue in the fibre.

II. **GELATINE, GLUE AND SIZE.**—These are three different forms of the same material, and are produced by the action of boiling water on collagen, the chemical individual, or individuals, of which hide fibre and the organic matter of bones ("osseine") are composed. Gelatine and glue differ solely in the care with which they are made, and therefore in the purity of the product; size is an impure gelatine put on to the market in the form of a jelly instead of that of a hard material.

Gelatine is now generally made from hide fibre, whilst bones form the raw material for glue, although in some factories both are made from either raw material.

The hide fibre used in the manufacture of gelatine is the waste cuttings of the tannery and skins that are not used for leather—*e.g.*, rabbit and dog skins which have been duly unhaired. The hide pieces are first well digested with dilute soda lye for some time in order to saponify completely the fat contained in them, then washed with cold water and bleached by sulphurous acid. The next process is to convert the collagen into gelatine, and to strain the solution from the unattacked elastin, &c. Several methods of doing this are in vogue: the material may be placed on the perforated false bottom of a kettle, into which water and steam are admitted, or it may be heated with a little water in earthenware vessels contained in a steam chest, and the solution of gelatine afterwards strained. It is sometimes customary to add a little albumin in the form of blood to the gelatine solution, in order that by its coagulation it may carry suspended matter to the surface in the form of a scum, which can be skimmed off. Whatever the plan for obtaining the solution of gelatine, it is desirable that this should be strong enough to set to a firm jelly on being run into the cooling troughs, since the subsequent heating to expel water impairs the gelatinising property of the product. The troughs are generally of such a shape that the blocks of gelatine may be directly sliced by wires into layers which are sufficiently thin to dry at the most advantageous speed, for it is in this drying that the greatest difficulty of gelatine manufacture is experienced. The sheets are placed upon netting and exposed to a drying atmosphere in two rooms. The first of these must be heated by closed steam pipes to a temperature not exceeding 20° C. = 68° F., lest the gelatine melt and run through the netting, or soften sufficiently to adhere strongly thereto. The air in this room must not be too dry, because if the sheets dry quickly at this stage they curl up and crack. The second room generally has a current of air forced through it, over the wire nettings, by means of an air propeller.

Gelatine contains from 0·5 to 2 per cent. of ash; its organic matter contains, per cent., C, 49·91; N, 17·72; H, 6·35; S, 0·50; O, 25·52. Good gelatine will gelatinise in a solution containing only 1 per cent.; but samples which have been long heated or contain much **chondrin** (the substance into which cartilage is converted by treatment similar to that which gelatine has undergone) will not gelatinise so well. Chondrin is precipitated from aqueous solution by acetic acid. All tannins precipitate gelatine solution.

Isinglass, used chiefly for clarifying wines, beer, &c., is obtained from the dried swimming bladder of various fishes; this membrane is washed, dried by exposure to air, and the inmost

layer stripped off and further dried. It contains some 86 to 93 per cent. of gelatine, up to 1·5 per cent. of ash, and a small proportion of insoluble matter. Much factitious isinglass is made from ordinary gelatine; it is, however, devoid of the true isinglass structure.

In making **glue** from bones, these are first steeped in hydrochloric acid (about 10 per cent. HCl)* until they are thoroughly soft, drained, washed and steamed in iron digesters at a pressure of 30 to 35 lbs. per square inch for three or four hours. The glue and fatty matter are run off from time to time into settling tanks kept hot enough to prevent gelatinisation; here the fat rises and is skimmed off (see *Bone fat*, Vol. II., p. 228), and any bleaching, such as with SO_2, which may be customary is effected. The glue is next filtered through sieves and boiled down by closed steam until it is capable of becoming a firm block when cold. This is cut up and dried as described for gelatine. The refuse in the digesters is sold as a manure material.

Size is prepared similarly to gelatine, but generally from much rougher material. It is commonly sent into the market as a stiff jelly.

Liquid glues are made by dissolving ordinary glue in acids. These prevent the solution from gelatinising when cold, but do not deteriorate the adhesive power of the dried material.

Such a liquid glue is made by dissolving 2 lbs. of glue in a quart of water and adding 7 ozs. of nitric acid (specific gravity 1·35). Acetic acid is also used.

Two flat surfaces of wood, glued together, should withstand a shearing stress of 38 to 73 kilos. per square centimetre, and a tensile stress of 14 to 37 kilos. per square centimetre.

Various glue substitutes are used as "cements" for china, &c. Solutions of casein in alkaline liquids, such as borax solution or soluble glass solution, are used for this purpose.

* The subsequent neutralisation of the acid with chalk precipitates a calcium phosphate containing 18 to 20 per cent. of P_2O_5; it is used as a manure.

CHAPTER XVII.

EXPLOSIVES AND MATCHES.

I. EXPLOSIVES.—Explosives are bodies which, under a suitable stimulus, yield suddenly large volumes of gas and evolve heat. Nearly all endothermic compounds are capable of behaving as explosives under suitable conditions. Thus, hydrogen peroxide, an endothermic substance, will explode when heated to the boiling point of water,

$$H_2O_2 = H_2O + O + 21{\cdot}5 \text{ Cal.},$$

that is, 34 grams (1 gram-molecule) of anhydrous hydrogen peroxide evolves, by its decomposition into water and oxygen, 21·5 kilogram units of heat. In actual practice, however, the heat of inter-combination of the elements constituting an explosive, provides the greater part, or the whole of the energy evolved by the explosive. Thus, the decomposition of mercuric fulminate into its elements, would be expressed by the equation—

$$HgC_2N_2O_2 = Hg + C_2 + N_2 + O_2 + 62{\cdot}9 \text{ Cal.};$$

but the actual energy evolved by its explosion is much greater, owing to the fact that the carbon and oxygen combine to form CO, with liberation of heat.

$$HgC_2N_2O_2 = 2CO + N_2 + Hg + 114{\cdot}5 \text{ Cal.}$$

It will be observed that, in both the cases quoted, the products are gaseous at the temperature of explosion. Seeing that the volume of these gases is large compared with the comparatively dense substances generating them (H_2O_2, specific gravity 1·45; $HgC_2N_2O_2$, specific gravity 4·42), the pressure exerted by the gases is great if they be confined in a space previously completely filled by the explosive from which they are derived.

For practical purposes the effective pressure exerted by an explosive depends upon—(1) the volume of gas at normal temperature and pressure liberated per unit volume of explosive, (2) the temperature attained at the moment of explosion and the coefficients of expansion of the gases, (3) the degree of imperviousness of the walls of the cavity in which the explosion occurs, and the rapidity with which the explosion takes place. When the thermal change accompanying an explosion and the

volume of gas are known, the total possible pressure can be calculated for an explosion taking place in an impermeable vessel, within the limits of our knowledge of the physical properties of gas at high temperatures. The effective pressure has been directly measured by performing the explosion in a closed vessel, which is either itself capable of permanent distortion (*e.g.*, a cylinder of lead), or communicates with pressure gauges, consisting of plungers bearing upon lead cylinders, the deformation of which serves as a measure of the pressure. A better method consists in firing the explosive from a pendulum mortar of known weight, and measuring the recoil produced. The difference between the calculated pressure and the effective pressure thus measured, depends largely on the rapidity of the explosion, a rapid explosive producing its maximum effect in a space of time sufficiently short to make the escape of gas from a not perfectly impervious envelope smaller than that which occurs during the action of a slow explosive. The rapidity of an explosive is the factor of most importance in deciding for what uses it is best fitted. Thus, for severe shattering action where the escape of gases cannot be fully restrained, an explosive like nitroglycerin, which is so rapid that the atmosphere itself is a sufficiently resistant envelope, is used, while for the slow movement of large masses—such as that involved in winning coal and propelling shot—gunpowder, which explodes comparatively slowly, is employed.

The rapidity of explosion is influenced by the state of division of the explosive as well as by its composition, whence it follows that, *ceteris paribus*, a compound will be a more rapid explosive than any mixture, however intimate. No distinction in kind can be drawn between the phenomenon of explosion and that of combustion, the difference being essentially one of rate of propagation. Thus it happens that a substance—*e.g.*, gun-cotton (*v.i.*)—may behave either as a combustible or as an explosive, according to the means used to initiate its decomposition. Loose gun cotton ignited by a source of heat of comparatively low temperature—as for example, a flame or red hot wire—merely burns, the hot gases generated by the combustion being able to escape freely, but should the gun cotton be ignited in the centre of a compact mass, the gases will not be able to escape readily, and the pressure rapidly generated will raise the temperature and cause approximately instantaneous combustion of the whole mass; the same effect is produced by the use of a source of initial high temperature and pressure—*e.g.*, a detonator of mercuric fulminate (*v.i.*). Detonation is, therefore, caused by the high pressure generated by the most rapid combustion that can be attained under any given conditions.

It follows from this that the theory that an explosion is necessarily initiated by the vibration of the particular wave

length generated by the detonator used, is erroneous, and, therefore, that so-called "sympathetic" explosion (the detonation of one explosive by the shock produced by the explosion of another in its neighbourhood) may be rather due to the setting up of a new vibration, probably identical with the vibration of the temperature of ignition of the second explosive, acted on sympathetically.

(A) Gunpowder.—Gunpowder is the oldest explosive known. It consists of a mixture of potassium nitrate, sulphur, and charcoal; its energy of explosion is derived from the exothermic reactions involved in the oxidation of the carbon and sulphur by the potassium nitrate. The original proportions in which these constituents were mixed were, in England, 75 per cent. of potassium nitrate, 10 per cent. of sulphur, and 15 per cent. of charcoal, the same proportion being still in use for black rifle powder. The manufacture of gunpowder comprises the preparation of pure potassium nitrate, distilled sulphur, and charcoal from a light wood such as alder, and the mixing of these to a homogeneous mass.

Potassium nitrate was at one time obtained exclusively from East Indian "**saltpetre earths**," which are natural accumulations of nitrates (the potassium, calcium and magnesium salts) in the surface soil, produced by the nitrification of nitrogenous organic matter through the agency of an organism (see *Manures*, Vol. II., p. 113). The earth varies in composition, the better kinds containing about 8 per cent. of potassium nitrate and some 4 per cent. of calcium nitrate. The earth is leached, and the liquor concentrated and mixed with wood ashes (crude potassium carbonate), whereby the nitrates are converted into the potassium salt, which crystallises, and in its crude state contains from 45 to 70 per cent. of KNO_3. It is generally recrystallised in India for exportation. The best quality (**Bengal ordinary**) contains 96·5 per cent. of KNO_3. The production of a saltpetre earth has formed an industry in some European countries, where it is made by mixing calcareous soil with putrefying nitrogenous substances, and allowing nitrification (for the mechanism of nitrification see *Artificial manures*, Vol. II., p. 113) to proceed for months or years.

For the manufacture of gunpowder the nitre is dissolved in boiling water and filtered hot. The hot liquid is constantly agitated; when its temperature falls to 32° C. = 90° F., the saltpetre crystallises in a fine "flour," and is drained and washed with successive small quantities of water; a further draining leaves the flour in a fit condition for the incorporating mill (*v.i.*). The greater part of saltpetre for gunpowder is now made by the decomposition of sodium nitrate (Chili saltpetre) and potassium chloride (from Stassfurt salts). Commercial sodium nitrate (95 per cent.) is dissolved together with Stassfurt "muriate of

potash" (which contains 80 per cent. of KCl) in the mother liquors of a previous crystallisation. The solution is boiled down and allowed to crystallise. Sodium chloride crystallises first, and the potassium nitrate is deposited on running the mother liquor into crystallising tanks. The flour thus obtained still contains some 8 per cent. of NaCl, and is purified by re-crystallisation and subsequent washing with water. Gunpowder saltpetre must be free from chlorides, which tend to keep it moist, and from sodium nitrate, which is also deliquescent. It is liable to contain potassium perchlorate, derived from Chili saltpetre. Beyond its use for gunpowder and fireworks, potassium nitrate is only employed for minor purposes—*e.g.*, as a preservative for meat.

Sulphur for gunpowder making is distilled in an iron retort, which is connected with a sublimation chamber, as well as with the condenser. At the beginning of the distillation the vapour is sent into the sublimation chamber, oxides of sulphur being thus got rid of; subsequently the vapour is passed through the condensers, and is collected as a liquid. The redistilled sulphur, which should be free from oxides of sulphur, is sent to the incorporating mill. The carbonisation of wood for gunpowder charcoal is effected with or without the collection of the bye-products (see *Destructive distillation*, Vol. II., p. 90), and at a temperature depending on the kind of powder to be made. The wood of the alder buckthorn (*Rhamnus frangula*) and that of the true alder and willow are preferred. The wood is stored for some three years before carbonisation, and is carbonised in cylinders fitting in cylindrical retorts. The resulting charcoal is stored for a couple of weeks before grinding, as it is then less liable to spontaneous ignition.

The temperature for the manufacture of black gunpowder charcoal ranges from 360° to 520° C. = 680° to 968° F., that for brown powder is carbonised at a lower temperature, 280° C. = 536° F., and in some cases is made from cereal straw. The temperature is also regulated according to the grain of the powder of which the charcoal is to form a part. The composition of some gunpowder charcoals is as follows (*Noble* and *Abel*):—

	Waltham Abbey Pebble.	Waltham Abbey Rifle Large Grain.	Waltham Abbey Rifle Fine Grain.
C, ...	85·26	80·32	75·72
H, ...	2·98	3·08	3·70
O and N, ...	10·16	14·75	18·84
Ash, ...	1·60	1·85	1·74

A high percentage of carbon corresponds with a high temperature of carbonisation. The sulphur and charcoal are ground separately and screened, and mixed with the still moist saltpetre in a rough mixing machine, consisting of a gunmetal drum and stirrer. This "green charge" is sifted, and passed to the incorporating mill, which consists of iron or stone edge-runners working on an iron or stone bed plate, the contact of iron with stone being avoided. During incorporation the mixture is kept moist. The "mill cake" thus produced contains from 1 to 6 per cent. of moisture, according to whether the grain to be made is small or large, and is then broken up between grooved gunmetal rollers, and pressed into cakes in gunmetal boxes lined with wood. The next process is "granulation," and is effected by passing the "press cake" between toothed rollers. The granulated cake is graded by sieves, and the powder is glazed by rotation in drums, an ounce of graphite to each 100 lbs. of the gunpowder being added for large grain powder. Drying and finishing by a final rotation in a cylindrical frame covered with canvas, for the purpose of removing dust, complete the process. The dust from the various grading processes is termed **meal powder**, and is much used in pyrotechny. "Pebble" and "prismatic" powders are cut from the press cake either by rollers provided with knife-like ridges, or by hand. **Prismatic powder** is generally perforated longitudinally to ensure uniformity of surface during combustion. The main portion of the energy set free in igniting gunpowder is derived from the oxidation of the charcoal by the saltpetre. The presence of sulphur is, however, necessary to increase the rapidity of explosion to such an extent as to allow of the exertion of a maximum of effective pressure. The low igniting point of sulphur (248° C. = 478° F.) adapts it for this purpose. The rapidity of explosion also depends on the size of grain, pebble or prismatic powder (*v.s.*) being used where a comparatively long continued pressure, as distinct from a sudden bursting strain, is required, as in heavy guns. Explosions of this type can be produced by powder poor in sulphur, in which class of material the charcoal used has to be carbonised at a low temperature and thus rendered more readily combustible. "Cocoa" powder, containing 79 per cent. of KNO_3, 2 per cent. of S, 18 per cent. of charcoal and 1 per cent. of moisture, is of this character. The brown colour is due to the lightly carbonised charcoal, which is generally made from straw. Mining powder, from which it is desired to obtain the highest possible effective pressure by generating a large volume of gas in a short space of time, contains about 67 per cent. KNO_3, 19 per cent. charcoal and 14 per cent. S. The increase in the proportion of sulphur also augments the inflammability of the powder. The chemical changes occurring in the explosion of gunpowder are very complex, and differ according to the composition of the powder.

The following equation (*Debus* and *Berthelot*) may be taken as showing the nature of the chief changes:—

$$16KNO_3 + 21C + 7S = 13CO_2 + 3CO + 16N + 5K_2CO_3 + K_2SO_4 + 2K_2S_2.$$

The salient properties of powders of various kinds are shown in the table below:—

	Cocoa.	Rifle, Large Grain.	Mining.
		1 kilogram of Dry Powder.	
Calories (kilogram degrees),	537	725·7	516·8
Litres of permanent gas at 0° C., and 760 mm.,	198	274·2	360·3

A comparison of the maximum pressure produced (in tons per square inch) by mining and black military powders, gave the figures 44 and 43 respectively, when the explosion was conducted in a closed vessel. The rapidity of the explosion of gunpowder is decreased by increase of apparent density, which varies from 1·67 for rifle powder, to 1·87 for brown prismatic powder. The exploding temperature of black powder is given at 300° C. = 572° F. At very low pressures—*e.g.*, 5 mm.—rapidity of explosion becomes very small, the converse being true of high pressures such as those obtaining in a gun.

Recently, the exigencies of modern warfare have caused the manufacture of smokeless, or as they are better termed in Germany, "rauchschwäche" powders. Inasmuch as the smoke of gunpowder consists chiefly of finely-divided potassium carbonate and sulphate, smokeless powders must not yield such saline products. Gun-cotton (*v.i.*) yields no solid matter on explosion, and is, therefore, smokeless, but is not adapted in its ordinary state for artillery and small arms, because of its intensely rapid and violent action.

Nitrated products of cellulose, containing less NO_3 than gun-cotton, are *per se*, too feeble, but when formed into a gelatinous solid with nitro-glycerin, give an explosion of the right character. For further information see *Nitro-Explosives*.

(*b*) **Nitro-Explosives—"High Explosives."**—These differ from gunpowder in that their explosive basis is a definite chemical compound, containing oxygen and oxidisable elements in unstable equilibrium. The expression nitro-explosive, although convenient, is a misnomer in the case of nitro-glycerin and gun-cotton, these compounds being the nitrates of certain organic radicles. Gun-cotton of ideal purity is cellulose hexanitrate, $C_{12}H_{14}O_4(NO_3)_6$, but as commercially prepared it contains various lower nitrates, although these do not exceed 2 to 3 per cent. in the best specimens.

The manufacture is conducted as follows:—The waste from cotton spinning machines is thoroughly freed from grease and dried at 80° C. = 176° F. It is introduced in charges of about 1 lb. into a cast-iron vessel containing 220 lbs. of a mixture of 1 part by weight of the strongest nitric acid, specific gravity 1·5, with 3 parts by weight of the strongest sulphuric acid. After some five or six minutes the cotton is placed upon a grating provided at the back of the nitrating vessel, and is compressed by a plate and lever. The charge, containing in its pores 10 to 15 times its weight of acid, is transferred to a covered stoneware pot, which is placed in a stream of cold water for twenty-four hours, at the end of which time nitration is complete. The bulk of the acid is removed from the cotton by a centrifugal machine, and the remainder is washed out by a cascade of water and another treatment in a centrifugal drier. Finally, two boilings by steam are administered. The gun-cotton is then pulped in a "beater," such as is used in paper manufacture. The pulp must be washed in a paddle machine, and after six hours, is tested according to the conventional method by heating 20 grains to 150° F. = 65° C. in a test tube, in which is suspended a piece of paper moistened with potassium iodide and starch. This paper must not be blued by the separation of iodine, indicating the evolution of nitrous fumes.

Gun-cotton is similar to cotton wool in appearance, but is somewhat harsher to the touch. Its specific gravity is 1·66 when its pores are freed from air. It is distinguished from the lower products of the nitration of cellulose by its insolubility in a mixture of ether and alcohol. It is soluble in ethyl acetate, and becomes converted into a jelly by nitrobenzene and nitroglycerin. In common with other explosive organic nitrates, it can be reconverted into the original substance—in this case cellulose—by treatment with potassium hydrosulphide. When kindled (as distinct from detonated) in an unconfined space, it burns fiercely with considerable flame (CO and H being evolved by its decomposition and burning in the air). It ignites spontaneously at about 150° C. = 302° F., but this temperature varies with the condition of the gun-cotton. It does not explode by percussive shock, but does so with shattering violence, even though saturated with water, when detonated with a cap containing mercuric fulminate. When wet, however, a priming of dry gun-cotton is advisable to ensure detonation. Its decomposition on explosion is represented by the following equation:—

$$C_{12}H_{14}O_4(NO_3)_6 = 5CO + 7CO_2 + 8H + 3H_2O + 6N.$$

It will be seen, therefore, that gun-cotton does not contain enough oxygen to yield completely oxidised products when exploded *per se*. If imperfectly washed, and containing a trace of acid, it is liable to spontaneous decomposition and explosion.

On explosion it gives more heat and more gas than an equal weight of any kind of gunpowder.

	Kilo. of gun-cotton yields
Calories (kilogram-degrees), ...	1071
Litres of gas, including water vapour, at 0° C. and 760 mm., ...	859

It is not of much industrial importance, as its price is too high; but it is used for loading torpedoes and for military mines. Attempts have been made to supply the oxygen required for its complete combustion by mixing it with nitrate. Thus tonite is made by mixing gun-cotton pulp (100 parts) with barium nitrate (79 parts). For sporting powders cellulose less highly nitrated than true gun-cotton is employed, as well as crude cellulose, such as sawdust, alone or mixed with metallic nitrates. Such substances are **E. C. Powder, Johnson's Powder,** and **Schultze's Powder.**

(*c*) **Nitroglycerin Explosives.**—Nitroglycerin, $C_3H_5(NO_3)_3$, is glyceryl trinitrate, and is prepared by acting on anhydrous glycerin (specific gravity 1·26) with a mixture of the strongest nitric and sulphuric acids (1 : 2 by volume), as in the preparation of gun-cotton. The mixture of acids is cooled and run into a leaden vessel kept cool by circulation of water through lead coils, and the glycerin is sprayed into the mixture by compressed air. The nitration takes place very rapidly, and the temperature is carefully regulated, so as not to exceed 30° C. = 86° F., as indicated by a thermometer in the liquid. Should the temperature rise unduly, there is risk of decomposition and even explosion. When the temperature has fallen, the contents of the vessel are run into a settling tank, the nitroglycerin then forming an upper layer; this is run off and washed, first with water and finally with dilute alkali, as residual traces of acid would cause its spontaneous decomposition. The acid from which the nitroglycerin has been separated is diluted with water, and a further portion of nitroglycerin obtained by allowing it to settle from the diluted acid. The yield is about 2 parts by weight of nitroglycerin from 1 of glycerin. On account of the difficulty of controlling the nitration of glycerin conducted as described above, a method known as the Boutmy-Faucher method has been devised, by which it is attempted to eliminate some of the heat of the reaction by a preliminary conversion of the glycerin into sulphoglyceric acid, $C_3H_5(HSO_4)_3$, with one-half of the sulphuric acid that is used in the direct treatment, thus removing a part of the water which would otherwise be split off during nitration, and evolve heat with the excess of sulphuric acid present. The rest of the sulphuric acid is mixed with the nitric acid, and the mixture cooled before use, as in the ordinary method.

Nitroglycerin is a colourless (though commercial samples generally have a shade of yellow) oily liquid, specific gravity 1·60, with a sweetish taste and toxic properties, producing faintness and headache. It is insoluble in water and solidifies at 8° C. = 46° F., and is volatile at 100° C. = 212° F. It is reconverted into glycerin by treatment with alkaline sulphides. When rapidly heated to 200° C. = 392° F. it inflames, but may detonate below this—*e.g.*, 180° C. = 356° F. Detonation is also caused by a shock or blow, and by the use of mercuric fulminate explosion takes place with certainty.

On explosion, nitroglycerin yields the following products :—

$$2(C_3H_5(NO_3)_3) = 6CO_2 + 5H_2O + 6N + O \quad ,$$

It will be seen, therefore, that nitroglycerin contains more than enough oxygen for the complete oxidation of its carbon and hydrogen, on which account it may be advantageously used in conjunction with explosives, such as gun-cotton, which contain less than the quantity of oxygen requisite for their complete oxidation (see *Blasting Gelatine*). The quantity of heat evolved, and of gas liberated by the explosion of one kilo. of nitroglycerin is—

Calories (kilogram degrees), ...	1,570
Litres of gas at 0° C. and 760 mm., including water vapour, ...	714

Nitroglycerin, therefore, gives less gas but more heat than does gun-cotton. In practice it is found that its effect is about five times that of an equal weight of blasting powder. The disadvantages attending the use of nitroglycerin, such as risk in transport, cause it to be little used; indeed in this country its sale and transport are illegal. When absorbed in a porous medium it becomes less unsafe to handle, and constitutes the class of explosives mentioned below.

Dynamite.—This explosive consists of nitroglycerin absorbed by an inert substance. The material generally used as an absorbent is a siliceous earth, **kieselguhr**, which consists of frustules of diatoms, and contains 95 per cent. of silica. Other absorbents, such as kaolin, chalk, magnesia, mica and cork charcoal, are used to a limited extent, but are less effective than kieselguhr. Kieselguhr is prepared by calcining and sifting the raw earth. It is then mixed by hand with three times its weight of nitroglycerin, forming a plastic mass of dynamite containing 75 per cent. of nitroglycerin and 25 per cent. of kieselguhr. The dynamite is then granulated by passage through a sieve, and made up into cartridges by the pressure of a wooden piston in a small metal cylinder, or by being expressed in a continuous rod, which is divided into suitable lengths; the finished cartridges are enclosed in parchment paper cases. Dynamite is less sensitive to shock than is nitroglycerin,

but like it, it is rapidly decomposed at 180° C. = 356° F. Small quantities, when kindled, may burn without explosion, but large amounts usually reach their critical temperature of explosion and then detonate. Frozen dynamite cannot be completely exploded when detonated with mercuric fulminate in the usual way, and has to be thawed before being used. Many accidents have occurred by carelessly heating frozen dynamite. As the specific heat of kieselguhr is about 0·2, an appreciable quantity of the energy generated on explosion of the nitroglycerin is uselessly employed in heating the absorbent.

The disadvantage of an inert absorbent and the fact that a certain amount of oxygen is set free in the explosion of nitroglycerin, have led to the manufacture of explosives of which the absorbent base is itself active. The following are the chief members of this class.

Blasting Gelatine.—This explosive consists of 93 per cent. of nitroglycerin, absorbed by 7 per cent. of nitrated cotton (collodion cotton containing lower products of nitration than the hexanitrate), this quantity sufficing for the surplus oxygen of the nitroglycerin. Blasting gelatine is made by warming nitroglycerin in a copper vessel, and stirring in the finely-divided nitrated cotton in small quantities at a time, the temperature being kept below 35° C. = 95° F. In the course of an hour the mass gelatinises to a viscous semi-transparent mass, which freezes at a low temperature. It can be employed under water, whereas dynamite is disintegrated when thus used, the nitroglycerin being washed out. It is somewhat sensitive to shock when frozen, but in its normal state requires a heavier detonating charge than does dynamite; its detonation also takes place more slowly. One kilo. of blasting gelatine liberates 1,530 Cal. on explosion. Its intensity of blasting effect is given as 160 when that of dynamite equals 100.

Gelatine dynamite consists of 65 per cent. of a thin blasting gelatine (containing 2·5 per cent. of nitrated cotton), 26·25 per cent. of potassium nitrate, 8·4 per cent. of wood meal and 0·35 per cent. of soda. Many other nitroglycerin explosives are made. **Cordite**, the smokeless powder adopted by the British Government, is of the blasting gelatine order, and is made by incorporating 58 parts of nitroglycerin with 37 parts of guncotton and reducing the mixture to a pulp by the addition of a solvent such as acetone (19·2 parts); the pulp is mixed with vaseline (5 parts) and manufactured into threads by expression through dies; the threads are used for loading cartridges.

(*d*) **Other Nitro-Explosives.**—The idea suggested by Sprengel of avoiding the transport of high explosives by supplying the user with two or more substances, each of which by itself is not explosive, to mix when required and thus yield an explosive composition, has received numerous developments.

The original explosives proposed by Sprengel were either solutions of such substances as nitrobenzene and picric acid dissolved in the strongest nitric acid, or porous cakes of potassium chlorate saturated with combustible liquids. These mixtures, which could be made on the spot, were detonated by mercuric fulminate. Thus, **hellhoffite** is a solution of nitro- and dinitrobenzene in nitric acid; **panclastite**, a mixture of nitrogen peroxide with carbon bisulphide. The objection to the handling of liquid explosives has caused a reversion to mixtures of solid substances, one class of which is oxidising agents and the other combustible materials, functioning in precisely the same manner as gunpowder, but needing a detonator for their explosion. Examples of this class of explosive are **roburite**, a mixture of dinitrobenzene, chloronitronaphthalene and ammonium nitrate, and **rack-a-rock** (potassium chlorate and nitrobenzene); also picric acid powders consisting of a mixture of a picrate with potassium nitrate or chlorate.

Picric acid is itself capable of detonation, and is said to be the main constituent of the French Government explosive, **Melinite.**

For *detonators*, **mercuric fulminate** is invariably employed. It is prepared by acting on 1 part by weight of mercury with 10 parts by weight of nitric acid in the cold, the solution being poured into 8·3 parts by weight of methylated spirit. A very violent action arises, and the fulminate separates in crystals, which are filtered off and washed. The finished product is a white crystalline powder, which is very easily exploded by friction or percussion unless it contains upwards of 10 per cent. of water. The detonation temperature is about 150° to 200° C. = 302° to 392° F. The equation representing the decomposition of mercuric fulminate on explosion, and information concerning the heat evolved, are given at the beginning of the chapter. For use for the caps of military and sporting cartridges, mercuric fulminate is generally mixed with a small quantity of potassium chlorate or nitrate.

II. **MATCHES.**—**Phosphorus.**—Two varieties of phosphorus of commercial importance are known, a vitreous pale yellow substance, crystallising in the regular system, and a red body, generally supposed to be amorphous, but recently alleged by Retgers to form hexagonal crystals. The former has a specific gravity of 1·83 and melts at 44° C. = 111° F. and boils at 290° C. = 554° F.; it is soluble in carbon bisulphide, is easily inflamed by friction, and oxidises spontaneously in air at the ordinary temperature. It is highly poisonous. The latter has a specific gravity of 2·14, and is not affected by heating in air below 290° C. = 554° F. when it becomes converted into the yellow variety. It is not readily inflamed by friction. It is insoluble in carbon bisulphide and is not poisonous. Both varieties are used for making lucifer matches.

In the manufacture of phosphorus the yellow variety is first obtained. The raw material is phosphoric acid, which is prepared from a mineral calcium phosphate (see *Manures*, Vol. II., p. 107). Formerly, phosphorus was made from bone-ash, but this source of supply is more costly than mineral phosphates. The finely ground mineral is mixed in a wooden vat with sufficient chamber vitriol (see *Sulphuric Acid*, Vol. II., p. 14) to convert all the lime of the mineral phosphate into calcium sulphate, the liquid being heated with open steam.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

When the reaction is complete, the contents of the vat is run into lead-lined filtering pans, and the solution of phosphoric acid, which should have a specific gravity of 1·17, is allowed to run through. The calcium sulphate is washed until the filtrate has a specific gravity of 1·01. The calcium sulphate retains some calcium phosphate, as shown by the following analysis (Readman), and is known as phosphatic gypsum :—

Calcium sulphate, ...	71·14
Calcium phosphate, ...	6·56
Siliceous matter, ...	12·10
Ferric oxide, alumina and organic matter, .	5·55
Water, ...	4·65
	100·00

It is used as a "drier" by manure makers. The liquor is evaporated in lead-lined tanks, containing lead worms through which high-pressure steam is passed, and provided with agitators. During the concentration, calcium sulphate is deposited and is removed by filtration.

The concentration is pushed until the liquor has a specific gravity of 1·325 to 1·5, according to the reducing agent subsequently used, the weaker liquor sufficing when sawdust is employed and the stronger being requisite for coke or charcoal, which are less absorbent. The phosphoric acid is now mixed with the reducing agent, which is some form of carbon, in quantity amounting to about 25 per cent., charcoal, coke, or sawdust being used as stated above. The wet mass has to be dried in iron pots or muffle furnaces, and is stored in airtight iron vessels until required for distillation. During the drying, the phosphoric acid loses water and becomes metaphosphoric acid (HPO_3). The distillation is carried out in bottle-shaped fireclay retorts about 3 × 1 ft. and 1 inch thick in the walls. The retorts, are placed in two tiers, in a furnace similar to that used in the distillation of zinc by the Belgian method (see *Zinc*, Vol. I., p. 183). Iron or copper tubes are affixed to the necks of the retorts by clay luting and are connected with the condenser, which is a long trough containing water beneath which the

aforesaid pipes open, and in which the phosphorus collects. The distillation is conducted at a high temperature and frequent breakages of the retorts occur. The chemistry of the distillation may be represented by the equation—

$$4HPO_3 + C_{12} = H_4 + 12CO + P_4.$$

The average yield of refined phosphorus is not more than 70 per cent. of the theoretical amount. The phosphorus which collects in the troughs, being fused, is ladled into boxes and transferred to the refinery, where it is re-melted, so that the sand and clay, with which it is mixed, separate, and the purified phosphorus is either squeezed through chamois leather or melted in a pan under a dilute solution of potassium bichromate and sulphuric acid. With this liquor it is agitated and heated by steam coils, and is finally washed with hot water, filtered through canvas and re-moulded into sticks or wedges, which are packed in water in tin-plate boxes for the market. On account of the high temperature needed for the reduction and distillation of phosphorus, externally fired retorts, such as have been described, are costly, as the heat has to be transmitted through their walls. Further, advantage cannot be taken of the possibility of displacing P_2O_5 by SiO_2 at high temperatures by using a charge of calcium phosphate, sand and carbon, and thus avoiding the preliminary manufacture of phosphoric acid, as the necessary temperature cannot be attained. On account of these drawbacks attending the use of retorts, internally fired furnaces present considerable *prima facie* advantages. An attempt to apply this principle in the form of the electric furnace (see *Aluminium*, Vol. I., p. 221) has been made by Readman and Parker, whose apparatus consists essentially of an iron box lined with fire-brick, provided with carbon electrodes at its lower part, and a hopper and feeding screw and an exit tube at the upper. The arc is established by small independent electrodes, and maintained by the large electrodes, phosphorus being volatilised in the ordinary manner. The charge consists of mineral phosphate, sand and coke, and it is claimed that a yield of 86 per cent. of the total phosphorus is obtained.

Red Phosphorus.—The manufacture of red phosphorus is conducted by heating ordinary phosphorus in a cast-iron pot heated at 240° to 250° C. = 464° to 482° F. by a sand bath. The pot is provided with a screw cover and a tube for the escape of air at the beginning of the operation. This tube is sometimes trapped with mercury or water, and is closed by a cock when the displacement of the air is complete. The conversion of yellow into red phosphorus takes place more rapidly when it is heated under pressure at 300° C. = 572° F., but the risk of the operation is greater than when a lower temperature is employed. By this process the yellow phosphorus is converted into hard

lumps of red phosphorus; grinding under water and extraction of unaltered yellow phosphorus by boiling under caustic soda solution, followed by thorough washing, finish the manufacture.

Matches.—The chief use of phosphorus, both yellow and red, is in the manufacture of matches, for which purpose it is adapted by its easy inflammability. The particular explosive mixture which is used for the heads of matches must be of such a nature that it can be ignited by slight friction, either on any rough surface or on one that has been specially prepared. Such sensitiveness is most easily attained by the use of phosphorus either for the head composition or for the prepared surface.

Matches may be roughly classified as "common" and "safety" matches, according as their ignition is due to the use of yellow or red phosphorus. In common matches phosphorus is the chief oxidisable constituent of the explosive mixture used for their heads, while in safety matches sulphur, generally in the form of antimony trisulphide, takes its place. The essential ingredients in a common match composition are:—(1) yellow phosphorus; (2) an oxidant, such as potassium chlorate or nitrate; (3) glue or gum, serving both as an emulsifying agent and as a binding material; (4) indifferent gritty material—*e.g.*, powdered glass, to increase friction; (5) colouring matter, such as ultramarine. The number of compositions in use is very great, but the following may be quoted as giving some idea of the proportions of the ingredients:—

Yellow phosphorus,	0·5	parts by	weight.
Potassium chlorate,	4·0	,,	,,
Glue,	2·0	,,	,,
Powdered glass,	4·0	,,	,,

The colouring matter varies according to the preference of the market for which the matches are intended.

The mixture is made by dissolving the glue and potassium chlorate in warm water, gradually stirring in the phosphorus to form an emulsion and adding the other ingredients. The composition is spread out on slabs heated by steam, and the match stem, whether of wood or wax-coated thread (for vestas), dipped therein to form the head. Wooden matches are generally primed by a preliminary dipping in sulphur or paraffin wax, which aids the ignition of the wood, the splints being made in double lengths and dipped at both ends. The dipped matches are allowed to dry, and are then halved and packed.

With safety matches red phosphorus is substituted for yellow, but usually on the prepared striking surface only.

Head Composition.		Rubber Composition.	
Antimony sulphide,	1	Red phosphorus,	2
Potassium chlorate,	1	Gum arabic,	1
Gum arabic,	2	Powdered glass,	1
Powdered glass,	12		

As an additional precaution, the stems of wooden safety matches are sometimes prepared by being soaked in a dilute solution of alum, magnesium sulphate or a phosphate, so that the wood may not glow after the match has been extinguished. The finished match is sometimes waterproofed with paraffin wax.

On account of the outcry against the risks run by operatives in match factories of contracting necrosis by exposure to the phosphorus vapour, attempts have been made to prepare matches entirely without phosphorus, but with indifferent success. The best composition hitherto proposed contains lead thiosulphate, PbS_2O_3, as the oxidisable ingredient, potassium chlorate serving as the oxidiser.

Fusees are common matches with wooden or wax stems, provided with enlarged heads consisting of powdered charcoal mixed with potassium nitrate and a binding material, tipped with an ordinary striking composition, the object of the former being to cause the match to burn fiercely in wind.

CHAPTER XVIII.

MINOR CHEMICAL MANUFACTURES.

THIS section is devoted to the chemistry of the manufacture of such acids, salts, &c., as are adjuncts to the processes described in the foregoing sections. They are, therefore, mainly manufacturers' and traders' chemicals, including such classes of substances as mordants for dyeing, solvents for oil extraction, and antiseptic chemicals for sewage treatment and food preservation.

I. **ACIDS.—Hydrofluoric Acid.**—This substance is chiefly used for etching glass, since it has the unique property of dissolving silicates of a refractory nature, such as glass. The principle of its application is the covering of the glass with a resistant varnish, which is then removed from the places to be etched, these being then subjected to the action of the acid, whereby the glass is dissolved and an etching, or a pattern in intaglio, produced. The pure aqueous acid produces clear markings on glass, whilst the gas or the aqueous acid containing a soluble fluoride gives a matt surface (see *Glass*, Vol. II., p. 160). Hydrofluoric acid has lately found an extending use as an antiseptic, particularly in brewing, but in the face of recent experiments by one of the authors, who found sodium fluoride to possess marked toxic properties, its employment should be adopted with considerable caution.

On account of the great insolubility of the fluorides of the alkaline earths, soluble salts of hydrofluoric acid—*e.g.*, sodium fluoride—have been used as softening agents for boiler waters (see Vol. I., p. 111), and the acid itself has been employed as a precipitant in sugar refining.

Antimony and chromium fluorides are used in dyeing and printing (see Vol. II., pp. 331, 332).

The manufacture of the acid is conducted on a comparatively small scale. Fluorspar is finely powdered, mixed with twice its weight of strong sulphuric acid and gently heated in a leaden retort; the gaseous hydrofluoric acid which is evolved is absorbed by water; $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. On account of the solvent action of HF on glass, the acid is preserved in leaden, platinum, guttapercha or "ceresin"* vessels. The

* This material is simply a grade of paraffin wax, and has lately been used to form bottles for pure hydrofluoric acid (see *Ozokerite*, Vol. II., p. 123).

commercial acid is usually very impure, containing silica and other solid matter in solution. The anhydrous acid, HF, is not an article of commerce.

Boric acid (*boracic acid*) is extensively used both as such, and as borax, $Na_2B_4O_7.10H_2O$, for minor industrial purposes—*e.g.*, the preparation of fusible glazes and special optical glasses; as a preservative of food, particularly milk and fish, and as a flux in metal working (see Vol. I., p. 35). Boric acid is a constituent of the pigment Guignet's green (p. 359), and of certain siccatives, such as manganese borate, for preparing drying oils. The free acid occurs naturally in steam emanating from volcanic formations, and is prepared from its salts—**tincal** (crude borax from Thibet), **Californian borax**, **boronatrocalcite** (the commercial "borate of lime," $Na_2B_4O_7.2CaB_4O_7.18H_2O$), obtained from Chili, **Stassfurtite** or **Stassfurt boracite**, $6MgO.8B_2O_3.MgCl_2$, and **pandermite** (*Turkish boracite*), $2CaO.3B_2O_3.4H_2O$.

In Tuscany the boric acid contained in steam of volcanic origin is collected by allowing the jets of steam (**soffioni**) to condense in reservoirs of water built round the point of issue. The water becomes gradually charged with boric acid, and is run into a common reservoir where it is allowed to settle, and is thence transferred into leaden pans heated by other soffioni. The less soluble impurities, the chief of which is calcium sulphate, are deposited in these pans, in which the liquid attains the specific gravity of 1·08, when it is run off and the boric acid allowed to crystallise. The crude acid (containing 80 to 90 per cent. of H_3BO_3) is purified by dissolution in water, treatment with animal charcoal and recrystallisation. The purified acid, H_3BO_3, forms unctuous crystals soluble in 25 parts of water at 15° C. = 60° F., and in 2·9 parts at 100° C. = 212° F. It loses water when heated to redness, becoming converted into the anhydride B_2O_3, a glassy transparent mass, which is fixed unless heated in a current of alcohol or water vapour. It is not as suitable as **borax** for use as a flux, for although metallic borates are readily formed by heating B_2O_3 with metallic oxides, such borates are generally insoluble in excess of B_2O_3, borax, on the other hand, dissolving these oxides completely. When used as a preservative, alone or in conjunction with salt, it appears to exercise but slight physiological action, no injurious effect having been definitely proved to arise from it; *per contra* it has not been shown to be thoroughly harmless. Its unacknowledged use, especially for milk, is illegitimate, in the absence of precise knowledge as to its action on the digestive organs of children or invalid persons.

Boric acid is also won by heating the better qualities of boronatrocalcite with hydrochloric acid in pitch pine vats, and crystallising the product. A similar process is used for Stassfurtite, save that sulphuric acid is employed in place of hydro-

chloric acid, the magnesium sulphate being recovered from the mother liquors. Pandermite is also treated in this manner.

Borax is chiefly prepared by recrystallisation of the natural crude borax, either in the form of tincal from Central Asia, or from California, the latter source being now the more important. It is also prepared by neutralising 1 part of boric acid with 1·1 to 1·2 parts of soda crystals; the soda is used in slight excess—but in insufficient amount to produce the metaborate ($NaBO_2.4H_2O$)—in order that the crystals may be well formed; to the same end the hot liquor is allowed to cool very slowly. The latter practice is general in refining borax, from whatever source it is obtained.

The deposits of crude borax found in California have an average composition of sand, 50 per cent.; sodium sulphate, 16 per cent.; sodium chloride, 12 per cent.; sodium carbonate, 10 per cent.; borax, 12 per cent. This material is worked up by simple dissolution in water, decantation from the insoluble matter and slow crystallisation, impure borax being thus deposited; this is recrystallised, yielding refined borax.

Another source of borax is **tiza**, $Na_2B_4O_7.2CaB_4O_7.18H_2O$. This is boiled with sodium carbonate in slight excess of the calculated quantity, calcium carbonate being formed and borax going into solution; the liquor is siphoned off and crystallised, yielding a crude borax containing 40 to 50 per cent. of pure borax, 40 per cent. of sodium sulphate* and 10 per cent. of sodium chloride.* Recrystallisation yields commercially pure borax.

Two forms of commercial borax are made, the ordinary **prismatic borax**, $Na_2B_4O_7.10H_2O$, manufactured by the above process, and an **octahedral** variety, $Na_2B_4O_7.5H_2O$, which is prepared by crystallising a strong solution, of specific gravity 1·246, the deposition of crystals beginning at 79° C. = 174° F., and ceasing at 56° C. = 133° F., below which prismatic borax begins to separate. The latter form is less common commercially than the former, although preferable to it in respect of the quantity of water it contains (diminishing cost of transport); it also fuses with less intumescence than does the prismatic borax, and is thus better fitted for use as a flux (see Vol. I., p. 35). It absorbs water from the air, becoming converted into the prismatic variety.

Arsenic Acid, H_3AsO_4.—The raw material for this substance is always arsenious anhydride, variously known as "**arsenious acid**," "**arsenic**," **white arsenic** (As_4O_6), which is a bye-product of the metallurgical treatment of arsenical pyrites and nickel and cobalt speiss (*q.v.*). The arsenic fume, condensed in the flues of the roasters used in smelting tin or copper ores (which usually contain arsenical pyrites), is mixed with soot (**arsenic soot**) when the roasting is conducted in direct contact with the

* Derived from impurities in the tiza.

furnace gases, but is free from this impurity when roasting in muffles is adopted. The white arsenic is purified by resublimation, either in a furnace fed with smokeless fuel, or in pots heated externally and connected by short flues to a condensing chamber sufficiently close to the furnace to reach the softening point of the sublimed white arsenic.* The glassy mass (**vitreous arsenic, arsenic glass**) thus obtained, becomes opaque and porcelain-like on keeping; it is generally ground for sale, and is used in glassmaking (*q.v.*), as an antiseptic for preserving skins, and, dissolved in glycerin, as a mordant in calico-printing.

The conversion of white arsenic into arsenic acid is effected by boiling 4 parts of As_4O_6 with 3 of nitric acid (specific gravity 1·35) and evaporating the solution to dryness. The oxides of nitrogen evolved in the process are oxidised by air in the presence of water, and the nitric acid is thus regenerated. Arsenic acid finds its greatest use as a substitute for tartaric acid in calico-printing, and as an oxidant in the preparation of rosaniline (*q.v.*).

Sodium arsenate is prepared directly by heating a mixture of white arsenic and sodium nitrate; the salt is used as a mordant.

Phosphoric acid, H_3PO_4, is prepared from a mineral phosphate as a preliminary to the manufacture of phosphorus (see *Explosives* and *Matches*, Vol. II., p. 409). It is sold in the form of a syrupy liquid, with about 80 per cent. of H_3PO_4, and usually contains traces of impurities derived from the mineral phosphate. When heated until white fumes are evolved, the liquid is converted into metaphosphoric acid (**glacial phosphoric acid**) which is used as a discharge in calico-printing.

Sodium phosphate is prepared by adding sodium carbonate to crude phosphoric acid, in the proportion indicated by the equation—

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + H_2O + CO_2.$$

Any lime present in the phosphoric acid is precipitated as carbonate and removed; the clear liquor is evaporated until it crystallises; the salt has the composition $Na_2HPO_4.12H_2O$, and is known as **rhombic phosphate of soda**, from the shape of its crystals.

Oxalic Acid, $H_2C_2O_4$.—This acid is a product of the oxidation of many non-nitrogenous organic matters. It is most easily prepared by the use of nitric acid as an oxidant, such diverse materials as sugar, woody fibre and hydrocarbons yielding a portion of their carbon as oxalic acid. Sugar, starch and nitric acid were the original raw materials, but in modern practice sawdust is oxidised by air in presence of caustic alkali. The best

* This incipient fusion is rendered possible by the fact that the sublimation takes place in an atmosphere of As_4O_6.

alkali, from the point of view of initial cost, would be caustic soda, but it is found that a yield of only 33 per cent., reckoned on the weight of the wood, is obtained when this alkali is used. When potash is employed, on the other hand, the yield rises to 81 per cent., and equal parts of potash and soda give almost the same yield (80 per cent.); a mixture is, therefore, always adopted. Soft woods, such as pine freed from resin by previous digestion with caustic soda solution, give the best results, as much as 95 per cent. of oxalic acid, reckoned on the weight of the dry wood taken, being obtained. Hard woods, such as oak, yield only 83 to 85 per cent. The alkaline liquor employed has a specific gravity of about 1·35, and is mixed with sawdust in the proportion of about 1 part of sawdust to 3 of mixed NaOH and KOH: the paste is spread in a thin layer on an iron plate heated in a furnace to a temperature of 250° C. = 482° F., until a uniform whitish melt results. This mass contains mixed oxalates, and is leached with water; the solution is evaporated until sodium oxalate crystallises and can be separated in centrifugal machines. The crude sodium oxalate is dissolved in boiling water, and the solution is heated with milk of lime for some hours; the liquor must be tolerably dilute to ensure decomposition of the sodium oxalate by the lime, the reverse reaction occurring in concentrated solutions (*cf. Causticising sodium carbonate; Alkali*, Vol. II., p. 30). The caustic liquor is drawn off from the calcium oxalate and used afresh; the calcium oxalate is decomposed with excess of sulphuric acid, $3H_2SO_4 : 1CaC_2O_4$; the calcium sulphate is filtered off and the solution concentrated; the rest of the calcium sulphate first separates, and fairly pure crystals of oxalic acid, $H_2C_2O_4.2H_2O$, then form. They are refined by recrystallisation; the mother liquors containing H_2SO_4 are used for the next batch.

The commercial acid may contain acid oxalates not completely decomposed by the sulphuric acid used in its preparation, and has been known to contain heavy metals—*e.g.*, lead. Sulphuric acid and sulphates may also be present. It can be sublimed, and is very poisonous. Oxalic acid is chiefly used in calico-printing as a discharge; it is also a solvent for Prussian blue, and thus forms the basis of some inks; it bleaches flax and straw; it is used as an acid detergent for articles made of copper and its alloys.

The acid oxalates of potassium (*Salts of sorrel, salts of lemon* KHC_2O_4 and $KHC_2O_4.H_2C_2O_4.2H_2O$) are made by adding to oxalic acid the appropriate quantities of potassium carbonate, and crystallising, and are used as domestic detergents.

Antimony potassium oxalate, $K_3Sb(C_2O_4)_3.6H_2O$, is used as a substitute for tartar emetic in calico-printing.

Lactic acid, $H_6C_3O_3$.—Of the isomerides, the ordinary lactic acid, or **ethylidene lactic acid**, $CH_3.CH(OH).COOH$, is that

commercially produced, and is generally prepared by the lactic fermentation of sugar or by treatment of invert sugar with caustic soda; the residue from whiskey stills, "pot ale," has also been suggested as a source (see *Brewing* and *Distilling*, Vol. II., p. 211). Lactic acid is isolated by conversion into calcium lactate, which is then treated with sulphuric acid. The commercial acid is a syrupy liquid of specific gravity 1·2. Its antimony salt is used as a substitute for tartar emetic in dyeing and calico-printing, and the acid itself may be used to replace more costly organic acids, such as tartaric and citric, in textile colouring.

Tartaric acid, $C_2H_2(OH)_2(COOH)_2$, is a bye-product in the manufacture of wine, being deposited as **argol**, crude bitartrate of potash (containing about 60 per cent., the rest being yeast refuse and organic debris deposited during fermentation), its deposition being favoured by the fact that bitartrate of potash is sparingly soluble in dilute alcohol. Much argol is extremely crude, and its content of tartaric acid has to be raised by recrystallisation before export, the product being known as **tartar**. This is worked up for tartaric acid by taking advantage of the insolubility of calcium tartrate and calcium sulphate. The crude tartar is boiled up with water containing chalk, half the tartaric acid being thus converted into the insoluble calcium tartrate; calcium sulphate is then added, giving calcium tartrate with the remaining half of the tartaric acid, previously present as neutral potassium tartrate. The total precipitate of calcium tartrate is strained through a sieve to remove wood fragments and similar gross impurities, and is then filter-pressed and washed. A treatment with sulphuric acid converts the precipitate into tartaric acid and calcium sulphate, the latter depositing and the former being drawn off and boiled down, preferably in a vacuum pan. An excess of sulphuric acid must be present to favour the formation of good crystals. The evaporation is generally conducted in lead vessels, causing contamination of the tartaric acid with this metal. The solution, separated from the calcium tartrate as described above, contains the potash of the original tartar as sulphate, and is evaporated for the recovery of this salt.

The commercial tartaric acid is the dextro-rotatory variety; three other tartaric acids exist, but are of no commercial importance. Ordinary tartaric acid is soluble in 0·7 part of cold and 0·5 part of boiling water; its aqueous solutions are gradually decomposed from the growth in them of fungus. It is used in dyeing and calico-printing, for effervescing medicines, baking powder and similar preparations. Calcium sulphate, free sulphuric acid and lead (as mentioned above) are apt to be present in commercial tartaric acid.

Citric acid, $C_3H_4(OH)(COOH)_3$, occurs in the acid juices of many fruits, but is commercially obtained from the lemon, the

lime and the bergamot. The fruits are pressed and the juice concentrated before importation into this country. Citric acid occurs to the extent of about 6 per cent. in lemon juice and 40 per cent. in the concentrated juice. The concentrated juice is run into a mixture of chalk and water, and the liquor is heated, calcium citrate being precipitated; after filtration the calcium citrate is treated similarly to the calcium tartrate obtained in the manufacture of tartaric acid (*v.s.*).

The commercial acid is liable to contain the same impurities as those in tartaric acid. Its uses are similar to those of tartaric acid.

Tartaric and citric acids intended for use as food or medicines should be free from lead. This impurity is found both as scraps of metal derived from the scraping of the pans used in concentration and also combined with the acid. Purification from lead is effected by conducting the preparation in the usual manner up to the first crystallisation of the acid, redissolving the product, treating it with sulphuretted hydrogen and completing the crystallisation in non-leaden vessels. Since lead sulphide is by no means completely insoluble in tartaric and citric acids, a better method would consist in the avoidance of the use of leaden vessels throughout the manufacture.

Benzoic acid, C_6H_5COOH, was originally prepared from gum benzoin—in which it exists already formed—by sublimation; that used for medical purposes is still prepared in this manner. It is also manufactured from hippuric acid, $CH_2NH(C_6H_5CO)COOH$, by boiling the urine of herbivoræ, which contains this acid, with strong hydrochloric acid; the hippuric acid undergoes hydrolysis according to the equation—

$$CH_2NH(C_6H_5CO)COOH + HOH = CH_2NH_2COOH + C_6H_5COOH.$$

Hippuric acid. Glycocoll. Benzoic acid.

The benzoic acid crystallises when the liquid cools, being sparingly soluble in cold water; the origin of the crude acid is suggested by its odour.

Much benzoic acid is now made from coal tar, toluene being chlorinated and the products hydrolysed by boiling with water under pressure. Most of the benzoic acid required for the manufacture of synthetic dyestuffs is obtained as a bye-product in the conversion of benzal chloride into benzaldehyde (*q.v.*), much of the benzaldehyde being oxidised during the process into benzoic acid or its calcium salt.

Salicylic acid, $C_6H_4(OH).COOH$, is obtained in limited quantity ("natural salicylic acid"), for special medical purposes, from methyl salicylate (**oil of wintergreen**) by hydrolysis. The bulk of the commercial acid is, however, prepared from phenol. This compound, C_6H_5OH, is converted into a phenylate by heating it with soda or lime, and the product is submitted to the action of

CO_2 at the ordinary temperature so long as the gas is absorbed; sodium phenyl carbonate, $CO(ONa)(OC_6H_5)$ (or the calcium salt), thus formed, is heated under pressure at 120° to 140° C. = 248° to 284° F. The resulting salicylate (*e.g.*, $C_6H_4(OH)COONa$), which is isomeric with the sodium phenyl carbonate, is converted into salicylic acid by treatment with HCl. The acid crystallises in needles and dissolves sparingly in cold water, but readily in hot water; it melts at 155° C. = 311° F. It is used in large quantities for preserving articles of food or drink. Its physiological harmlessness is not beyond question.

Saccharine is a benzoic acid derivative, used as a sweetening agent. It is prepared by treating toluene with sulphuric acid at a temperature not exceeding 100° C. = 212° F., when a mixture of ortho- and para-toluene sulphonic acids, $C_6H_4(CH_3)SO_2OH$, in about equal proportions, is formed. The mixture is oxidised with dilute nitric acid, yielding the corresponding benzoic acids, $C_6H_4(COOH)SO_2OH$. The potassium salts of these acids are treated with phosphorus pentachloride, giving chlorides of the form, $C_6H_4(COCl)SO_2Cl$. On treating these bodies with ammonia, the para-derivative yields the diamide, $C_6H_4(CONH_2)SO_2NH_2$, whilst the ortho-compound gives **ammonium orthosuphamidobenzoate**,

$$C_6H_4(SO_2NH_2)COONH_4.$$

These are separated by the greater solubility of the latter in water; its aqueous solution when decomposed with an acid, yields saccharine, $C_6H_4\begin{<}\begin{matrix}CO\\SO_2\end{matrix}\begin{>}NH$, **anhydro-orthosulphamidobenzoic acid.** Several similar sweetening substances are now synthesised commercially.

II. **SALTS.—Chromates and Bichromates.**—The source of chromium for the manufacture of these salts is invariably **chrome iron ore** (*chromite*), which, when pure, is a ferrous chromite, $FeO.Cr_2O_3$; average samples contain 40 to 50 per cent. Cr_2O_3. The FeO is often replaced by other oxides of the same type, especially MgO, as seen in the following example:—Cr_2O_3, 51·20; Al_2O_3, 12·80; Fe_2O_3, 1·45; FeO, 13·32; MgO, 12·55; CaO, 3·15; SiO_2, 4·95; CO_2, 0·20 per cent.

The preparation of chromates from this material depends upon the fact that Cr_2O_3 in the presence of air and a strong base, is readily converted into chromic anhydride, CrO_3, which forms a chromate with the base. It will be obvious that the cheapest base to use is lime, but soda ash (Na_2CO_3) is generally employed as an auxiliary to render the mass plastic when hot, and thus aid reaction. About 6 parts of ore, 3 of chalk or limestone, and 3 of soda ash are finely ground and intimately mixed, and roasted in a reverberatory furnace provided with a terraced bed, in order that

the charge, by being rabbled from one bed to the other, may be subjected to a gradually increasing temperature, and fresh surfaces may be exposed to the air. Gentle heating is requisite at first (this occurring on the highest portion of the bed) to prevent fluxing before efficient oxidation has taken place. When this operation is properly conducted, conversion into chromate is almost perfect, the essential reaction being expressed by the following equation:—

$$2(FeO.Cr_2O_3) + 4CaO + O_7 = Fe_2O_3 + 4CaCrO_4,$$

the roasted mass is removed from the furnace, when it consists largely of calcium chromate and sodium chromate, together with ferric oxide, derived from the oxidation of the ferrous oxide of the ore; it is then heated with a solution of soda ash, whereby the calcium chromate is transformed into the sodium salt, Na_2CrO_4,* and the calcium left as carbonate. The solution is filter-pressed from the sludge, and evaporated until a specific gravity of 1·5 is reached. Sulphuric acid is then added in quantity sufficient to convert the sodium chromate into bichromate, anhydrous sodium sulphate being thrown down; the solution is evaporated until **sodium bichromate**, $Na_2Cr_2O_7.2H_2O$, crystallises. The yield is about 90 per cent. of the calculated quantity. The salt is deliquescent, and on this account its purification by washing is less easy than is that of the corresponding potassium salt; it is usually separated from the mother liquor by a centrifugal machine and dried. It is often stated that a monetary advantage arises from the use of sodium instead of potassium bichromate, on account of the lower atomic weight of sodium increasing the percentage content of CrO_3; this is erroneous, since the sodium salt crystallises with 2 mols. of water, and has a molecular weight slightly greater than that of the potassium salt, which is anhydrous. The real advantage is due entirely to the difference in price of the two salts, owing to the cost of sodium salts being lower than that of the corresponding potassium salts.

Potassium bichromate, $K_2Cr_2O_7$, is prepared by double decomposition of sodium bichromate with potassium chloride. It crystallises in large orange anhydrous crystals, which are easily purified by washing or by crystallisation, on account of their moderate solubility.

A modification of the method described above for obtaining chromate from chrome iron ore consists in utilising the property of calcium chloride to form a flux for lime, and to induce its union with anhydrides at a moderate temperature.

A finely-powdered mixture of the ore and limestone is made into a paste with slaked lime and calcium chloride solution; the

* Na_2CrO_4 crystallises with 10 mols. of water, and is isomorphous with Glauber's salt, $Na_2SO_4.10H_2O$.

paste is moulded into bricks, which are fired in a kiln to causticise the lime and thus cause their texture to be porous from the escape of CO_2. It is claimed that exposure to air after firing completes the oxidation, so that the bricks can be systematically leached, and the very soluble calcium chloride washed out, accompanied by comparatively little of the less soluble calcium chromate, which can be converted into the sodium or potassium salt in the usual manner.

A suggestion has lately been made for preparing bichromate from chromate by electrolysis, the bichromate appearing at the anode and caustic alkali at the cathode.

Chromic anhydride, commonly called "**Chromic acid**," CrO_3, is prepared by pouring a cold saturated solution of $K_2Cr_2O_7$ into strong sulphuric acid with constant stirring; the CrO_3 separates in crystals. It is customary to substitute the crude calcium chromate for the potassium salt. Owing to the method of preparation it is frequently contaminated with sulphuric acid. The crystals are deliquescent.

For other chromates see *Pigments*, Vol. II., Chap. XV.

Manganates and Permanganates.—Manganates are produced by the ignition of any compound of manganese in the presence of air, and in contact with a strong base. The action proceeds most readily with an alkali, although baryta will serve the same purpose, and is indeed used in the preparation of Cassel's green, a pigment consisting of barium manganate. An equation to represent the formation of sodium manganate, from the cheapest form of manganese, the dioxide, is given below:—

$$MnO_2 + 2NaOH + O_2 = Na_2MnO_4 + H_2O.$$

More rapid and vigorous oxidation can be secured by the use of other oxidants than air—*e.g.*, nitrate or chlorate.

The alkali manganates prepared in this way are stable in strongly alkaline solutions; such solutions of manganates are green; manganates cannot be crystallised from solution, however, because in pure water they break up in the following manner:—

$$3Na_2MnO_4 + 2H_2O = Na_2Mn_2O_8 + MnO_2 + 4NaOH.*$$

Sodium permanganate, thus formed, is not easily crystallised, but the potassium salt, $K_2Mn_2O_8$, crystallises readily in red prisms; it is similarly prepared. The manganates and permanganates are used as oxidising agents; thus sodium manganate, being the cheapest, serves as a disinfectant. When the alkalinity

* The whole of the manganese can be obtained as a permanganate by treating the manganate with chlorine or bromine, thus:—

$$2K_2MnO_4 + Cl_2 = 2KCl + K_2Mn_2O_8.$$

Compare the production of K_3FeCy_6 from K_4FeCy_6.

essential to the preservation of a manganate is objectionable, **potassium permanganate** is substituted for the sodium salt, as it can be prepared in a state of purity. Potassium permanganate is also used for producing manganese brown (hydrated MnO_2) on cotton fabrics, and also for staining wood; both uses depend on the ease with which permanganates are reduced by organic substances.

Sulphates.—Blue Vitriol or **Blue Stone, Copper Sulphate,** $CuSO_4.5H_2O$.—This salt is mainly a bye-product and may be prepared in a variety of ways according to the raw material available. Thus it may be prepared by the direct dissolution of copper in sulphuric acid, as in the parting of gold from silver and copper by the action of boiling oil of vitriol. When silver and gold alone are parted by sulphuric acid, the silver is recovered by precipitation with copper, an equivalent of copper sulphate being formed; a considerable quantity of pure copper sulphate is thus obtained. In order to save acid when copper sulphate is the main product, the preparation may be effected by treating granulated copper, spread on the perforated false bottom of a suitable vessel, with a spray of dilute sulphuric acid, which gradually attacks the copper in presence of air; the copper being oxidised at the expense of the air instead of at that of the sulphuric acid.

Advantage is also taken of the ease with which copper sulphide can be oxidised to sulphate by air at a dull red heat. Thus scrap copper may be heated with sulphur and then oxidised by roasting, or crude sulphide of copper obtained in the dry process of winning copper may be similarly oxidised. Copper sulphate from this source is liable to contain both iron and nickel. When a product free from iron is required, the temperature of the roasting is raised to such a point that any sulphate of iron is decomposed, leaving ferric oxide as an insoluble residue easily separated from the copper sulphate. Sulphates other than ferric sulphate—*e.g.*, $ZnSO_4.7H_2O$—have a strong tendency to crystallise with copper sulphate and form mixed salts. This arises from the fact that the members of the class of sulphates known archaically as the **vitriols**, tend to crystallise with the same number of molecules of water, either $7H_2O$ or $5H_2O$, and to assume the same form. Since ferric sulphate is not a "vitriol," iron may be separated from copper sulphate by oxidation and crystallisation. The chief uses of copper sulphate are the preparation of agricultural germicides, the production of a black dye with logwood, and the preparation of electrolytic baths.

Ferrous Sulphate, Copperas, or **Green Vitriol,** $FeSO_4.7H_2O$.—The chief supply of sulphate of iron is obtained as a bye-product in the manufacture of cement copper, by precipitating this metal from a solution of its sulphate by means of scrap iron (see *Copper*, Vol. I., p. 165). It is also obtained by the direct treatment of

iron scrap with sulphuric acid, especially the spent acid left after the process of purifying mineral oils (*q.v.*). It is, moreover, a bye-product of the manufacture of alum by the oxidation of pyritic shale. The ferrous sulphide left by distilling iron pyrites for the sake of obtaining a fraction of its sulphur (see *Sulphur*, Vol. II., p. 1) is also weathered and leached for ferrous sulphate.

The solution, however obtained, is allowed to crystallise on wooden rods, and is put upon the market as green vitriol.

Black vitriol is a term applied to a highly crude sulphate of iron containing the sulphates of copper and nickel and some ferric sulphate. It is a bye-product in the precipitation of copper in the Mansfeld process. An artificial "black vitriol" is prepared by staining common green vitriol with a little gallo-tannic acid.

Green vitriol readily oxidises in air, losing water at the same time and becoming converted into basic iron sulphate, brown in colour and incompletely soluble in water. When crystallised from an acid solution its tendency to oxidise is diminished.

The chief uses of ferrous sulphate are as a co-colouring matter for logwood (*q.v.*), as a sewage preciptant and disinfectant, for making inks and as a reducing agent—*e.g.*, in the preparation of the indigo vat. It is soluble in about one and a-half times its weight of cold water.

Ferric sulphate, $Fe_2(SO_4)_3$, is now prepared to some extent by the oxidation of pyrites and treatment with sulphuric acid, the product being used as a substitute for aluminium sulphate for the defecation of sewage.

Zinc sulphate, white vitriol, $ZnSO_4.7H_2O$, may be prepared by leaching roasted zinc sulphide or by dissolving zinc scrap in sulphuric acid. It finds a limited use in the preparation of pigments—*e.g.*, Orr's white zinc (*q.v.*)—in calico-printing and dyeing, and as a drier for oils (*q.v.*); its use in pharmacy is chiefly as an astringent.

Aluminium Sulphate.—This is used both *per se* and in the form of alum. The name **alum** primarily applies to potassium aluminium sulphate, $KAl(SO_4)_2.12H_2O$, but has been extended in significance to all salts of the type $R'R'''(SO_4)_2.12H_2O$ which are isomorphous.

Alum can be prepared from most minerals rich in alumina, but a few offer special advantages. Particularly is this the case with the mineral known as **alum stone** (*alunite*), which contains an anhydrous double sulphate of aluminium and potassium associated with aluminium hydroxide. An analysis of such material is as follows:—

	Per cent.
SiO_2,	13·4
Al_2O_3,	35·5
K_2O,	12·5
SO_3,	30·0
Fe_2O_3,	0·05
H_2O,	8·5

The preparation of alum is effected by roasting this alum stone at a temperature of about 500° C. = 932° F., and extracting the roasted product with sulphuric acid (specific gravity 1·5), the solution being then allowed to crystallise. When water is used to leach the roasted stone, the basic double sulphate of the form $K_2O.SO_3.Al_2O_3.2SO_3$ is formed; this crystallises in cubes instead of the octahedra characteristic of ordinary alum, and on account of its basic constitution is neutral in reaction, whereas ordinary alum is acid to litmus. On this account it is used in some cases where acidity is objectionable.

Pyritic shale is another source from which alum can be prepared. Some of this, particularly that of South Lancashire, is sufficiently carbonaceous to serve as its own fuel in the burning process necessary to bring about the oxidation of the pyrites destined to furnish the sulphuric acid which attacks the aluminous material (clay). The sulphate of alumina thus formed is extracted by systematic leaching. As a portion of the sulphur remains in the form of ferrous sulphide, after roasting, long exposure to air before leaching is advisable, so that the oxidation of this ferrous sulphide may yield ferrous sulphate, which is useful in the conversion of the aluminium sulphate into alum (*v.i.*). The solution of crude aluminium sulphate is evaporated in tanks over which the hot gases of a reverberatory furnace are led, and when sufficiently concentrated (*e.g.*, specific gravity 1·4), the solution is transferred to precipitating tanks and treated with potassium chloride or sulphate, alum being thrown down. Potassium chloride (the cheaper material) can be used when sufficient sulphate of iron is present to yield with it potassium sulphate and iron chloride. The crude precipitate is purified by crystallisation. Alum is chiefly prepared nowadays from **aluminium sulphate**, which is manufactured by decomposing clay with sulphuric acid.

The clay should be free from calcium carbonate, which consumes H_2SO_4 uselessly. When a "fat" clay—*e.g.*, china clay—is used, it should be dehydrated by gentle roasting to render it porous. It is treated with H_2SO_4 (specific gravity 1·5) in lead pans, and the mass allowed to solidify; this is either sold as **alum cake**, containing the bulk of the silica of the clay, or it may be purified and sold as sulphate of alumina, or used for the preparation of alum.

Alum contains about 10 per cent. of alumina; alum cake contains about 12 per cent. of Al_2O_3 and 22 per cent. SiO_2. The chief advantage of alum is that, having been crystallised, it is purer than other aluminous products. For most purposes both alum and alum cake should be as free as possible from iron and uncombined sulphuric acid. **Burnt alum** is calcined alum.

Alum and aluminium sulphate are used chiefly by the dyer as mordants; they are also employed by the paper maker and the leather dresser.

Ammonia alum, $NH_4Al(SO_4)_2.12H_2O$, is similarly prepared, $(NH_4)_2SO_4$ being substituted for K_2SO_4 in the process.

Chrome alum, potassium chromium sulphate, $KCr(SO_4)_2.12H_2O$, is strictly analogous in composition and crystalline form to common alum. It is obtained as a bye-product in the manufacture of alizarin by the oxidation of anthracene with potassium bichromate and sulphuric acid (see *Alizarin*, Vol. II., p. 281). It is used as a mordant, and for rendering substances containing gelatine insoluble.

Potash Salts.—The main source of potassium salts, at the present day, is the deposit found at Stassfurt, near Magdeburg. The salts there found appear to have resulted from the evaporation of sea water, which has successively deposited the salts it contains in an order determined by their solubility, relative abundance and mutual reactions. The salts last to be separated constitute Stassfurt salts, and their occurrence as an isolated patch in a bed of the commoner salts of sea water, extending over a much more considerable area, is to be accounted for by the escape of the bulk of the mother liquor from the remainder of the area, this having been brought about by geological disturbances. Many double salts occur in the Stassfurt deposits. The chief are **carnallite**, $KCl.MgCl_2.6H_2O$, **kainite**, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$, **kieserite**, $MgSO_4.H_2O$, **anhydrite**, $CaSO_4$, associated with large quantities of **rock salt**, NaCl, and various minor salts, viz. :—**polyhalite**, $MgSO_4,K_2SO_4.2CaSO_4.2H_2O$, **boracite**, $6MgO.8B_2O_3.MgCl_2$, &c.

The general principles of separation adopted for all these salts depend on the alteration of the solubility of each salt by the influence of the accompanying salts, and the separation thus induced either of a simple salt or of some double salt. By varying the conditions, selective separations can be favoured. The chief raw material is crude carnallite, which contains about 60 per cent. of pure carnallite, 20 per cent. of common salt and 15 per cent. of kieserite, the balance consisting chiefly of anhydrite.

The process now generally adopted of obtaining **potassium chloride** from carnallite, consists in treating the crude material with a solution containing about 20 per cent. of $MgCl_2$ (obtained as a mother liquor from previous operations). The carnallite alone is dissolved in considerable quantity, and the solution thus obtained deposits on cooling crystals which are mainly KCl. These are purified by systematic washing, and when dried contain from 80 to 90 per cent. of KCl.

The mother liquors from the potassium chloride are evaporated in pans, having flues passing through the liquid in the manner of a locomotive boiler. Sodium chloride first separates in crusts which settle on the bottom, thus rendering heating from below undesirable, and the mother liquor yields artificial

carnallite (returned to the main process) on cooling. The final residual liquid is rich in magnesium chloride, and is worked up for bromine.

The residue left in the first extraction of the crude carnallite is mainly common salt (50 to 55 per cent.), with much kieserite (25 per cent.), some potassium and magnesium chlorides and a good deal of anhydrite (10 per cent.). The sludge is chiefly valuable for the magnesium sulphate, which it contains in the form of kieserite, that salt being insoluble in water until it passes into the form of Epsom salts, $MgSO_4 7H_2O$, a transition delayed by the presence of magnesium chloride in the water. By washing this sludge with water on to an inclined sieve, the bulk of the water flows away whilst sufficient passes over the surface of the sieve with the sludge to react slowly with the kieserite to form cakes of **block-kieserite**, containing $MgSO_4.3H_2O$ and some insoluble matter, mainly $CaSO_4$.

Kieserite sludge is also worked up for Glauber's salts by treating it with an equivalent quantity of NaCl, which at a temperature of about 0° C. = 32° F. enters into double decomposition on account of the sparing solubility of $Na_2SO_4.10H_2O$ (**Glauber's salt**) at low temperatures. This process can only be carried out in winter, unless it be practicable to cool artificially.

The large quantity of magnesium chloride obtained as a bye-product in the manufacture of potash salts, finds little application, although attempts have been made to use it as a source of chlorine, as in the Pechiney process (*q.v.*).

Potassium sulphate is sometimes prepared from kainite—the chief market for which, however, is in the raw state as a manure—by treatment with KCl, which reacts with the $MgSO_4$, forming magnesium chloride and potassium sulphate, this last-named salt being easily crystallised from the liquor. It is used as a manure and a source of potassium salts.

The final mother liquor from the working up of the Stassfurt salts is used for the preparation of bromine (*q.v.*).

Although Stassfurt salts yield a large proportion of the potash salts of commerce, yet considerable quantities are obtained from other sources, the chief being **wood ashes, residues from beet sugar** and **suint**. Sources of purely mineral character are **sea water, orthoclase** and **potash mica**.

Potassium chloride is but little used as such, but serves as a starting-point for the preparation of most other potash salts. An example of its use is afforded by the conversion of sodium into potassium nitrate in the manufacture of gunpowder (Vol. II., p. 400).

Potassium Carbonate, or **Potashes**, K_2CO_3.—The conversion of KCl into K_2CO_3 is effected by the Leblanc process (see *Soda ash*, Vol. II., p. 19), which is worked in the same manner as that used for soda, with a few modifications, due to the greater

chemical activity of the base. Thus, muffles (blind roasters) are not used in the conversion of the chloride into sulphate, because of the high temperature requisite.

The decomposition of potassium sulphate in the revolver, corresponding with the black-ash process, is less easily effected, and the product attacks the lining more readily than does black ash. The extraction of the roasted product is performed as for soda, and the liquor is evaporated to the point at which K_2SO_4 separates, followed by K_4FeCy_6 (resulting from the interaction of the potash, iron—present as an impurity—and the carbon and nitrogen of the coal). The crude ferrocyanide is recrystallised for the market. The mother liquor is evaporated to dryness and calcined in a reverberatory furnace. Sometimes the liquors are carbonated before calcination, when the product contains some 87 per cent. of K_2CO_3, and is marketable; otherwise the crude potash is leached out and separated from insoluble impurities, and the solution evaporated to dryness. Such refined potash contains about 98 per cent. of potash, calculated as K_2CO_3.

Caustic potash, KOH, is prepared from K_2CO_3 by causticising with lime in the same manner as is practised for caustic soda; it is used chiefly for making soft soap, and for preparing oxalic acid (*q.v.*).

In America, Russia and Scandinavia much potash is made from **wood ashes**. The percentage of potash varies with the nature of the wood, being, for instance, about 0·4 per cent. in pine wood, and 0·15 in oak wood; in most cases, however, the percentage *on the ash* is about the same—viz., 10 per cent. The wood ash is systematically extracted in wooden vessels fitted with perfected false bottoms, and the liquor, containing about 25 per cent. of salts, is evaporated in cast-iron pots; the residue is calcined. A good deal of sulphate is removed during evaporation. The crude potash may be purified in the manner described above; on an average it contains 60 per cent. of K_2CO_3, the balance consisting of KCl, K_2SO_4, and Na_2CO_3.

A large quantity of potash is obtained from the residues left after the extraction of sugar from beet. The beet molasses contain the total potash salts of the root, amounting to 0·5 per cent., calculated on the weight of the root. This material is either ashed directly, yielding **schlempekohle**, or it is desaccharised or fermented (see *Beet Sugar*, Vol. II., p. 173), and the final liquors (**vinasse** or **schlempe**) from these processes is evaporated to dryness and the residue calcined. Instead of this direct conversion into a char, it is sometimes customary to destructively distil the liquor, whereby it is carbonised, and much ammonia, methyl alcohol and trimethylamine come over from the organic constituents, which are rich in nitrogen. By further heating the trimethylamine hydrochloride—obtained by absorbing the gas

in hydrochloric acid and evaporating the liquor until the less soluble ammonium chloride has crystallised—much methyl chloride is obtained, and is condensed by pressure for the use of the synthetic colour manufacturer.

The final char, however obtained, is a black porous mass containing about 30 per cent. of K_2CO_3 and 20 per cent. of Na_2CO_3, the remaining soluble salts consisting chiefly of K_2SO_4 and KCl. The liquor obtained by leaching the char is evaporated in iron pans heated by steam coils, until K_2SO_4 crystallises, from which the mother liquor is run off; further evaporation causes the crystallisation of KCl, this and the sulphate being sold as such or used for making K_2CO_3 by the Leblanc process. The mother liquor is further concentrated until $Na_2CO_3.H_2O$ separates in the hot liquid, which is run off, and on cooling deposits more KCl. The next salt to separate is the double carbonate, $K_2CO_3.Na_2CO_3.12H_2O$, which is returned to a fresh quantity of the liquor or is decomposed by a second crystallisation. The final mother liquor is taken to dryness and calcined for potassium carbonate, the product containing about 85 per cent. K_2CO_3 and 8 per cent. Na_2CO_3.

Another source of potash is the "yolk" or "suint" of wool, resulting from the sweat of the animal. The raw wool is systematically extracted with cold water, whereby the potash soaps, together with some of the neutral fat and cholesterol, are extracted. The solution is evaporated to dryness and calcined, giving a residue containing about 85 per cent. of K_2CO_3, the remainder being Na_2CO_3, together with K_2SO_4 and KCl. This crude potash may be purified in the usual way.

Strontium Salts.—Strontium occurs both as carbonate (**strontianite**, $SrCO_3$) and sulphate (**cœlestine**, $SrSO_4$). These minerals are worked up for strontium nitrate and hydrate, the sole compounds of this metal which are of technical importance.

Strontium nitrate, $Sr(NO_3)_2$, is prepared by dissolving the carbonate in nitric acid. If the native carbonate can be procured sufficiently free from other bases, which would consume nitric acid, this mineral may be used. The carbonate is sometimes made from cœlestine by fusing it with soda ash and leaching out the sodium sulphate formed by the double decomposition $SrSO_4 + Na_2CO_3 = SrCO_3 + Na_2SO_4$.

Strontium nitrate dissolves in twice its weight of water at the ordinary temperature, and in its own weight at 100° C. = 212° F. It is much used in pyrotechny for the sake of the red colour which it imparts to a flame.

Strontium hydrate, $Sr(OH)_2$, is now largely employed in sugar refining (Vol. II., p. 175). Strontium carbonate can be burnt to strontia (strontium oxide, SrO) just as calcium carbonate can be burnt to lime; but the temperature required is very much higher than that at which limestone can be burnt. By heating

the carbonate in superheated steam, it can be directly converted into hydrate at a low red heat.

More generally, strontium hydrate is produced from the sulphate; the conversion is not easy, and many processes have consequently been devised to effect it. Cœlestine is roasted with equal weights of coal and iron oxide (brown iron ore); strontium sulphide is probably formed, for when the mass is lixiviated with water, ferrous sulphide remains undissolved, whilst the solution contains strontium hydrate.

$$SrSO_4 + C_4 = SrS + 4CO\,;\ Fe_2O_3 + C = 2FeO + CO.$$
$$SrS + FeO + H_2O = Sr(OH)_2 + FeS.$$

By another process, cœlestine is ground, mixed with coal and roasted to sulphide; the sulphide is extracted with water, and the solution mixed with caustic soda solution. The reactions involved may be represented by the equations—

$$(1)\ 2SrS + 2H_2O = Sr(OH)_2 + Sr(SH)_2\,;$$
$$(2)\ Sr(SH)_2 + 2NaOH = Sr(OH)_2 + 2NaSH.$$

The strontium hydrate crystallises from the liquor, and is recrystallised; the sodium hydrosulphide is converted into carbonate by passing CO_2 through the mother liquor, and causticised for further use.

Strontium hydrate crystallises from water in the form $Sr(OH)_2.8H_2O$, dissolving in 50 parts of cold water and 2·4 parts of boiling water. It is less poisonous than barium hydrate.

Barium salts are prepared from the native carbonate (**witherite**), and sulphate (**heavy spar**) by processes analogous to those used for strontium. Barium chloride, $BaCl_2.2H_2O$, is used to a certain extent for softening water for boiler use (see Vol. I., p. 111), and barium carbonate for decomposing objectionable sulphates in clay intended for the preparation of tiles and similar goods. Soluble barium salts are strongly toxic.

III. **HALOGENS.—Bromine.**—The chief source of bromine is the end liquors of the separation by crystallisation of the salts from sea water or of the Stassfurt deposits. Sea water contains about 2 ozs. of bromine per ton, whilst the mother liquor from the working up of carnallite in the Stassfurt process contains as much as ¼ per cent. of bromine or 5½ lbs. per ton. The preparation from these liquors is dependent upon the fact that bromine is more readily expelled from its salts than is chlorine by a suitable oxidising agent in the presence of an acid. It was at one time customary to distil the liquor with such an oxidising agent—viz., manganese dioxide and sulphuric acid. Nowadays, however, chlorine is generated from MnO_2 and HCl in a separate still, and the liquors are treated systematically with the gas, the bromine being liberated. The concentrated liquor, containing the bromine chiefly as $MgBr_2$, trickles into a tower fitted

with a perforated plate, serving to distribute the liquid over a large number of earthenware balls with which the tower is filled;* this packing is supported by a perforated false bottom, beneath which the chlorine enters. The bromine liberated from the liquor as it meets the ascending chlorine, passes through an exit pipe at the upper end of the tower, and is condensed in a stoneware worm. The partly spent liquor, still containing some bromine and chloride of bromine, passes into another vessel, which remains full of the liquid since the outlet for the completely spent liquor is brought up from the bottom to the level of the top of the vessel. Steam is blown into the bottom of this vessel and is distributed by baffle plates; by this means the remainder of the bromine is expelled chiefly as bromine chloride, and passes up the tower together with the fresh chlorine, which enters at the top of the heating vessel. By adopting this second vessel, not only is the liquid freed from bromine, but the bromine chloride which it yields is, to a great extent, decomposed by contact with fresh magnesium bromide in the tower. After the main quantity of bromine has been condensed in the stoneware worm, the residual vapour is caught in a small tower packed with iron borings and is thus held in the form of ferrous bromide, from which the bromine can be recovered in a marketable form (potassium bromide) by double decomposition with potassium carbonate.

The crude bromine contains chloride of bromine, and generally lead bromide and hydrocarbons, the latter being derived from tar joints. It is shaken with potassium bromide, to decompose bromine chloride, and distilled in glass retorts.

Bromine is chiefly used for the production of bromeosins (*q.v.*) and for the manufacture of bromides. On account of the difficulty of transporting liquid bromine it is sometimes absorbed in kieselguhr, the product being termed "solidified bromine."

Potassium bromide, KBr, is prepared by acting on iron with bromine to form an iron bromide, which is then run into a hot solution of potassium carbonate, whereby an oxide of iron is precipitated and CO_2 liberated, while potassium bromide remains in solution and is crystallised. It is used as a sedative and for making silver bromide on photographic plates.

Iodine is a characteristic constituent of seaweed, but its production from the ash of such plants (**kelp**) is now much diminished by the competition caused by the preparation of iodine as a bye-product in the manufacture of nitrate of soda (p. 112). The method of isolating iodine from the mother liquor of the crystallisation of **caliche** (p. 112) is as follows:—The mother liquor contains about 0·5 per cent. of iodine, chiefly as sodium iodate

* A Lunge plate column (see *Vitriol Making*, Vol. II., p. 8) would probably be effective.

($NaIO_3$).* It is run into wooden vats coated with pitch, and treated with the calculated quantity of a solution prepared by passing SO_2 into sodium carbonate solution until there has been formed a sulphite of sufficiently acid structure to ensure the saturation of the whole of the soda of the iodate with SO_2. An agitator is provided in order that the liquids may be thoroughly mixed, whereupon the iodine separates according to the equations—

(1) $2NaIO_3 + 2NaHSO_3 = 2Na_2SO_3 + 2HIO_3$.

(2) $2HIO_3 + 5Na_2SO_3 = 5Na_2SO_4 + I_2 + H_2O$.

The sparing solubility of iodine in water allows of its direct recovery by subsidence; the iodine which remains in solution is fixed by the addition of a small quantity of sodium bisulphite and sodium carbonate, and the liquor is returned to the boiler in which the caliche is first extracted. The crude iodine is filter-pressed, when it contains about 80 per cent. I, 10 per cent. of water and 10 per cent. fixed matter. It is generally refined by sublimation in iron retorts with stoneware condensers, and comes into the market containing 98 per cent. I.

The applications of iodine are not sufficiently numerous to create a demand commensurate with the supply, on which account its price is a conventional one. Iodine is used for the preparation of iodeosins (*q.v.*) and other synthetic dyestuffs, as well as in medicine and in making iodides, which are also used in medicine and in photography.

Potassium iodide, KI, is made, like the bromide, by taking advantage of the direct combination of iodine with iron. The compound formed appears to be Fe_3I_8, which is a better compound for the purpose than FeI_2, since the iron is more readily separated than from the ferrous salt by double decomposition with an alkali carbonate.

IV. **CYANOGEN COMPOUNDS.**—The heat of formation of cyanogen is $C_2,N_2 = -65{\cdot}7$ Cal., from which it may be anticipated that direct union of C and N can only be effected at a high temperature. Since the compound has acidic properties, the presence of a metal capable of forming a powerful base—*e.g.*, K or Ba—favours the production of cyanogen from its constituents. It is thus possible to produce a cyanide at a temperature below that essential for the formation of free cyanogen. This circumstance is taken advantage of in a process which has been worked experimentally on a large scale and consists in heating a mixture of barium carbonate with carbon, in the form of pitch, in a fireclay retort through which nitrogen is passed, while the temperature is kept at about 1,400° C.

* Highly oxidised substances are characteristic of Chili saltpetre; thus, in addition to nitrate, iodate and chromate, perchlorate has lately been recognised.

= 2,552° F. by a producer-gas furnace. Since barium cyanide is acted on by CO_2 at high temperatures, the nitrogen used must be free from this gas, and may be conveniently obtained as the waste gases from the carbonating towers of the ammonia-soda process (*q.v.*). The use of ammonia as a source of nitrogen for preparing cyanides has not hitherto proved feasible. Another method of some promise consists in removing the sulphur of a thiocyanate—*e.g.*, NaCyS (*v.i.*)—by means of zinc or other metal combining readily with S. A fairly cheap source of nitrogen for the formation of cyanides, and one which has the advantage of being already in union with carbon, is waste animal matter—*e.g.*, leather cuttings, blood and the like. When such material is heated with potassium carbonate and iron borings, a cyanogen compound is formed. The potassium carbonate and iron are heated in a cast-iron pan set on the hearth of a reverberatory furnace, the organic matter* being introduced after the fusion of the mass. Oxidation should be prevented by maintaining a reducing atmosphere. The "metal" thus produced is lixiviated with boiling water, and the crude liquor is evaporated until **potassium ferrocyanide** (*yellow prussiate of potash*), $K_4FeCy_6 . 3H_2O$, crystallises out. The mother liquor is evaporated to dryness and returned to the process, and the crude prussiate is recrystallised. The carbonaceous matter left after extraction is used for decolorising paraffin wax and vaseline. The reactions which prevail during this process are somewhat obscure. It appears that sulphur is necessary for their occurrence, and is present in the organic matter and the crude potash used. The potash reacts with the carbon and nitrogen of the organic matter, yielding KCN, which in its turn acts on iron compounds, notably FeS, formed in the melt, according to the equation—

$$6KCy + FeS = K_2S + K_4FeCy_6.$$

The products of the destructive distillation of coal contain cyanogen, which, therefore, forms a bye-product of gas manufacture. On the Continent, purification of gas by hydrated ferric oxide is chiefly practised, and the cyanogen is thus fixed, chiefly as Prussian blue (ferrocyanide of iron), while a portion exists as ammonium thiocyanate. The iron oxide mass is worked up as follows:—It is systematically extracted with warm water, and the ammonium thiocyanate recovered by crystallisation. The extracted residue is dried, mixed with caustic lime, and heated in closed vessels by means of steam, calcium ferrocyanide being formed. This salt is extracted with water and treated with KCl in the boiling solution, whereby the double salt CaK_2FeCy_6 is precipitated. This is heated with a solution of K_2CO_3, when $CaCO_3$ and K_4FeCy_6 are formed; the dilute liquors are boiled

* This is usually previously charred.

down in a vacuum pan, and crystallised prussiate, $K_4FeCy_6.3H_2O$, is obtained.

Potassium ferrocyanide is chiefly used for the preparation of potassium cyanide (*v.i.*), Prussian blue, and potassium ferricyanide, K_3FeCy_6.

Potassium ferricyanide (*red prussiate of potash*), K_3FeCy_6, is made by removing an atom of potassium from the ferrocyanide by means of an oxidising agent, thus—

$$K_4FeCy_6 + Cl = KCl + K_3FeCy_6;$$

bromine and lead peroxide can also be used. This salt is used in dyeing and calico-printing, chiefly as an oxidant, and in photography.

Potassium cyanide, KCN, is generally obtained from the ferrocyanide, though much is now prepared from the sulphocyanide. When K_4FeCy_6 is dehydrated and fused, it is decomposed according to the equation, $K_4FeCy_6 = 4KCy + Fe + C_2 + N_2$. Much cyanogen is thus lost, and a more economical process consists in the addition of potassium carbonate, when the reaction takes place thus—

$$K_4FeCy_6 + K_2CO_3 = 5KCy + KCyO + Fe + CO_2.$$

In this case the product is a mixture of cyanide and cyanate. Since this latter is of small commercial value, attempts are made to suppress it by the introduction of charcoal into the fusion, $KCNO + C = KCN + CO$. The fused mass is allowed to settle, and the clear melt poured off.

Potassium cyanide is chiefly used as a solvent for gold in extracting that metal from ores which contain it in a sufficiently finely-divided condition; as a solvent for gold and silver in electroplating and gilding baths.*

Potassium sulphocyanide or **thiocyanate**, KCSN, is prepared from the ammonium salt as a raw material, which is obtained as a bye-product in gas manufacture. The insolubility of cuprous thiocyanate is sometimes taken advantage of in separating sulphocyanide from gas liquor. A method proposed for the preparation of sulphocyanides, analogous to that by which they are probably formed among the products of the distillation of coal, is that of allowing ammonia to react with CS_2, according to the equation $CS_2 + 4NH_3 = NH_4CNS + (NH_4)_2S$.

V. **SOLVENTS.**—For purposes where aqueous liquids cannot be employed as solvents, certain liquid compounds of carbon are pressed into service. An ideal solvent must be volatile without change at a moderate temperature, so as to be easily recoverable,

* The modern product, said to be made by the process represented by the equation, $K_4FeCy_6 + Na_2 = 4KCy + 2NaCy + Fe$, consists largely of sodium cyanide, and may, therefore, appear to contain more than 100 per cent. of KCy if the Cy alone be used as a basis of assay.

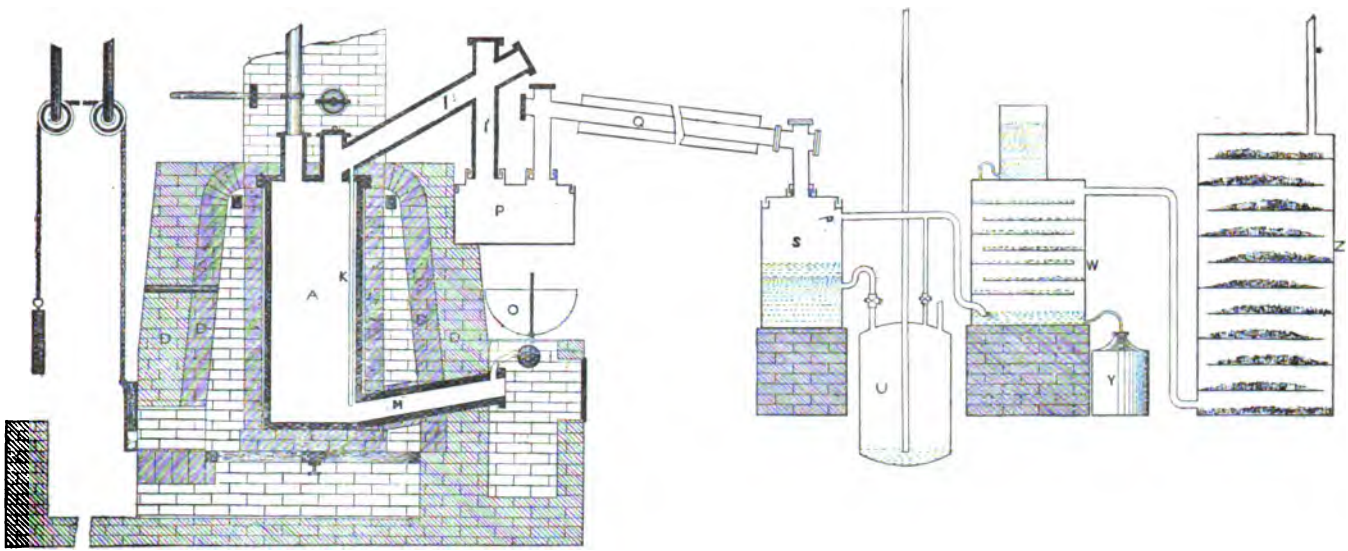


Fig. 43.—Carbon bisulphide retort.

A, Retort; D, furnace; N, side inlet; O, vessel containing molten sulphur; I, escape pipe; K, pipe leading to retort; P, vessel for catching sulphur; Q, condenser; S, receiver; W, apparatus for catching residual vapours; Y, oil collectors; Z, oxide purifier.

non-inflammable and non-poisonous. Few solvents fulfil all these conditions.

Carbon Bisulphide, CS_2.—This compound is an excellent solvent for fats and for sulphur, but is both inflammable and poisonous. It boils at 46·5° C. = 116° F., and inflames in air at about 150° C. = 302° F.; not only is the vapour itself poisonous, but the products of combustion CO_2 and SO_2 are also noxious.

CS_2 is an endothermic compound, its heat of formation being $C,S_2 = -26$ Cal. On this account its production, by the direct union of its elements, can only be attained at a high temperature. The operation is generally conducted in a vertical cast-iron retort, A (Fig. 43), set in a furnace, D, and provided with a side inlet, N, through which molten sulphur is allowed to flow from the vessel O.

Charcoal, preferably prepared from waste wood, spent dye wood and the like, is filled into the retort and brought to a cherry red heat before the introduction of the sulphur. The CS_2 formed escapes by the pipe I, which slopes upwards to permit uncombined sulphur to condense and flow back down the pipe K, to the bottom of the retort. Any sulphur which is carried on is caught in the vessel P, whilst CS_2 passes down a long Liebig's condenser, Q, where it is chilled by the water-jacket and is caught in the receiver S. The closed vessel U is employed for forcing the condensed CS_2, by means of compressed air, into a storage tank. Residual vapours are caught in the apparatus W, being scrubbed out with oil dribbling over a series of trays; on heating the oil, collected in Y, in a retort, the CS_2 can be recovered and the oil used again. Permanent gases, such as H_2S, are suppressed by passage through the lime and iron oxide purifier Z.

The crude CS_2 is purified by agitation with lime water, and distillation with a small quantity of any fixed oil and a little lead acetate, the object being to retain objectionable sulphur compounds. The process of purification is completed by rectification.

Commercial CS_2 has a nauseous odour, but the pure substance has an ethereal smell. Its specific gravity is 1·29.

An apparatus fitted for the obtainment or recovery of oils from seeds and waste products has been shown at p. 230. The solvent is also used in vulcanising caoutchouc (*q.v.*).

Carbon Tetrachloride, CCl_4.—This liquid is in some ways preferable to CS_2, as it is uninflammable, less poisonous and has a higher boiling point, 77° C. = 171° F. Its specific gravity is 1·63. It is at present prepared from CS_2, and is, therefore, more costly than that solvent.

It may be obtained by passing a mixture of CS_2 vapour and chlorine through a red-hot tube; or by the action of chlorine on CS_2 at the ordinary temperature, in the presence of iodine or of

antimony pentachloride. Sulphur chloride, SCl_2, is a product of the reaction, and remains dissolved in the CCl_4, from which it is removed by treatment with lime.

Commercial CCl_4 constantly contains CS_2, from incomplete conversion. Other solvents, such as **benzene**, **benzine** (**benzoline**), other forms of light petroleum and **alcohol** have already received notice.

BIBLIOGRAPHY.

MATERIALS OF CONSTRUCTION.

Redgrave (G. R.) Calcareous Cements. London.

Thurston (R. H.) Materials of Engineering. New York.

Thurston (R. H.) Text-book of the Materials of Construction. New York.

Unwin (W. C.) Testing of Materials of Construction. London.

Journal of the Iron and Steel Institute.

Minutes of the Proceedings of the Institution of Civil Engineers.

SOURCES OF ENERGY AND STEAM RAISING.

Borchers (W.) Elektro-Metallurgie. Braunschweig. English Translation by W. G. M'Millan. London.

Butterfield (W. J. A.) Gas Manufacture. London.

Donkin (B.) Gas, Oil, and Air Engines. London.

Gore (G.) The Electrolytic Separation of Metals. London.

Fischer (F.) Die Chemische Technologie des Wassers. Braunschweig.

Jamieson (A.) Text-book on Steam and Steam Engines. Eleventh edition.

Mills (E. J.) and Rowan (J.) Fuel and its Applications. London.

Ostwald (W.) Elektrochemie. Leipzig.

Rankine (W. J. M.) A Manual of the Steam Engine and Other Prime Movers. London. Thirteenth Edition.

Schoop (P.) Die Secundär-Elemente. Halle.

Schwackhöfer (F.) and Browne (W. R.) Fuel and Water. London.

Thorpe (T. E.) *Dictionary of Applied Chemistry.* Art. "Fuel." London.

The Electrician.

LUBRICATION.

Allen (A. H.) Commercial Organic Analysis. Vol. ii. London.

Redwood (B.) and Holloway (G. T.) Petroleum. London.

Thurston (R. H.) Treatise on Friction and Lost Work in Machinery and Millwork. New York.

Thurston (R. H.) Friction and Lubrication. New York.

METALLURGY.

Bloxam (C. L.) and Huntingdon (A. K.) Metals. London.
Borchers (W.) Elektro-Metallurgie. Braunschweig. English Translation under the title of "Electric Smelting and Refining," by W. G. M'Millan. London.
Eissler (M.) The Metallurgy of Gold. London.
Eissler (M.) The Metallurgy of Silver. London.
Fischer (F.) *Chemische Technologie.* Section "Metallurgie."
Gore (G.) The Art of Electrometallurgy. London.
Howe (H.) The Metallurgy of Steel. New York.
M'Millan (W. G.) Electro-Metallurgy. London.
Percy (J.) Metallurgy. London.
Phillips (J. A.) and Bauerman (H.) Elements of Metallurgy. London.
Roberts-Austen (W. C.) An Introduction to the Study of Metallurgy. London. Third Edition.
Rose (T. K.) The Metallurgy of Gold. London. Second Edition.
Turner (T.) The Metallurgy of Iron. London.
Williams (M.) The Chemistry of Iron and Steel Making. London.

SULPHURIC ACID MANUFACTURE.

Lunge (G.) Sulphuric Acid and Alkali. Vol. i. London.
Thorpe (T. E.) *Dictionary of Applied Chemistry.* Art. "Sulphuric Acid." London.

ALKALI AND ITS BYE-PRODUCTS.

Lunge (G.) Sulphuric Acid and Alkali. Vols. ii. and iii. London.

DESTRUCTIVE DISTILLATION.

Butterfield (W. J. A.) Gas Manufacture. London.
Lunge (G.) Distillation of Coal Tar and Ammonia. London.
Mills (E. J.) Destructive Distillation. London.
Mills (E. J.) and Rowan (J.) Fuel and its Applications. London.
The Journal of Gas Lighting.

ARTIFICIAL MANURE MANUFACTURE.

Spon's *Encyclopædia of the Industrial Arts.* Art. "Manure." London.
Thorpe (T. E.) *Dictionary of Applied Chemistry.* Art. "Manures, Artificial." London.

PETROLEUM.

Redwood (B.) and Holloway (G. T.) Petroleum. London.

LIME AND CEMENTS; CLAY INDUSTRIES AND GLASS.

Benrath (H. E.) Die Glasfabrication. Braunschweig.
Chatelier (H. Le). Recherches Expérimentales sur la constitution des mortiers hydrauliques.

Church (A. H.) Pottery and Porcelain. London.
Fischer (F.) *Chemische Technologie.* Section "Thonindustrie."
Redgrave (G. R.) Calcareous Cements. London.
Shenstone (W. A.) Chemical Glass Blowing. London.
Thonindustrie Zeitung.
Verein deutscher Portland-cement. Fabrikation der Portland-cement. Berlin.

SUGAR AND STARCH.

Birnbaum (K.) Die Fabrikation der Stärke. Braunschweig.
Lock (C. G. W.) and Newlands Bros. Sugar. London.
Lock (C. G. W.), Wigner (G. W.), and Harland (R. H.) Sugar Growing and Refining. London.
Thorpe (T. E.) *Dictionary of Applied Chemistry.* Arts. "Sugar" and "Starch." London.

BREWING AND DISTILLING.

Jörgensen (A.) Micro-organisms and Fermentation. London.
Maercker (M.) Handbuch der Spiritusfabrikation.
Moritz (E. R.) and Morris (G. H.) A Text-book of the Science of Brewing. London.
Otto (F. J.) Die Bierbrauerei, Branntweinbrennerei und Liqueurfabrikation. Braunschweig.
Thorpe (T. E.) *Dictionary of Applied Chemistry.* Art. "Brewing." London.

OILS, RESINS, AND VARNISHES; SOAP AND CANDLES.

Allen (A. H.) Commercial Organic Analysis. Vol. ii. London.
Benedikt (R.) and Lewkowitsch (J.) Oils, Fats, and Waxes. London.
Cameron (J.) Oils and Varnishes. London.
Carpenter (W. L.) and Leask (H.) A Treatise on the Manufacture of Soap, Candles, Lubricants, and Glycerine. London.
Groves (C. E.) and Thorp (W.) Chemical Technology. Vol. ii. London.
Schaedler (C.) Die Untersuchungen der Fette, Oele, Wachsarten und der technischen Fettproducte. Leipzig.
Wright (Alder). Fixed Oils, Fats, Butters, and Waxes. London.

TEXTILES AND BLEACHING; COLOURING MATTERS, DYEING AND PRINTING.

Duerr (Geo.) Bleaching and Calico-Printing. London.
Gardner (J.) Bleaching, Dyeing, and Calico-Printing. London.
Hummel (J. J.) The Dyeing of Textile Fabrics. London.
Knecht (E.) and Benedikt (R.) The Chemistry of the Coal-tar Colours. London.
Knecht (E.), Rawson (C.), and Loewenthal (R.) A Manual of Dyeing. London.
Nietzki (R.) The Chemistry of Organic Dyestuffs. London.

Schultz (G.) and Julius (P.) Systematic Summary of Organic Colouring Matters. London.

Witt (D. N.) Chemische Technologie der Gespinnstfasern.

PAPER AND PASTEBOARD.

Cross (C. E.) and Bevan (E. J.) A Text-Book of Paper Making. London.

PIGMENTS AND PAINTS.

Church (A. H.) The Chemistry of Paints and Painting. London.

Hurst (G. H.) Painters' Colours, Oils, and Varnishes. London. Second Edition.

LEATHER, GLUE, AND SIZE.

Davis (C. T.) Leather Manufacture. Philadelphia.

Dawidowsky (F.) A Practical Treatise on the Fabrication of Glue. Philadelphia.

Heinzerling (C.) Grundzüge der Lederbereitung. Braunschweig.

Knapp (F.) Natur und Wesenheit der Gerberei des Leders. München.

Procter (H. R.) A Text-Book of Tanning. London.

Trimble (H.) The Tannins. Philadelphia.

EXPLOSIVES AND MATCHES.

Guttman (O.) Manufacture of Explosives. London.

Thorpe (T. E.) *Dictionary of Applied Chemistry.* Art. "Matches." London.

GENERAL REFERENCES.

Fischer's *Chemische Technologie.*

Groves and Thorp's *Chemical Technology.* London.

Spon's *Encyclopædia of Industrial Arts and Manufactures.* London.

Thorpe's *Dictionary of Applied Chemistry.* London.

Journal of the Society of Chemical Industry. London.

Dingler's *Polytechnische Journal.* Stuttgart.

INDEX.

A

ABEL'S test of flashing point of oils, 121.
Abies canadensis, 378.
Abietic acid, 242; anhydride, 242.
Absinthe, 215.
Absolute alcohol, 217; strength O.P., 218.
Absorbents for nitro-glycerin, 406.
Absorption of gases by charcoal, 92; tannin by hides, 395.
Acacia catechu, 378.
Acer saccharinum, 177.
Acetanilide, Preparation of, 316.
Acetate, aluminium, Preparation of, 360.
Acetate, Amyl, 217; Basic copper, 359; of lime, Brown, 95; of lime, Grey, 93, 95.
Acetic acid, 219; Application of, in cotton printing, 340; Factitious vinegar from, 222; Ferment, 219; from spent lye in esparto boiling, 345; Percentage of, in vinegar, 221; used in bleaching, 267; in dyeing, 232; Yield of, by distillation of wood, 95.
Acetic fermentation, 219; Succinic acid produced in, 219.
Acetification, 219; Conditions of, 221.
Aceto-arsenite of copper, 359.
Acetone, 94.
Acetylene, Action of, on copper, 74; Enriching gas by, 74; from calcium carbide, Yield of, 74; Heat of formation of, 74; Illuminating value of, 74; Liquid, 74; Specific gravity of, 74.
Acid colours, Dyeing cotton with, 334; Dyeing silk with, 339.
Acid, "drips" in vitriol chambers, 14; dyes, 330; dyes classified, 336; egg, 8; for etching on glass, 160, 413; green, 336; in tan liquors, 379; magenta, 288, 336; mordants, 331; oxalates of potassium, 417; "tar," 78.
Acids, fatty, Formulæ of, 223; Melting point of, 223; volatile, with steam, 227.
Acids, Iso-linolenic series of, 226; Linoleic series of, 226; Linolenic series of, 226; Oleic series of, 226, 228; Ricinoleic series of, 226.
Acorn galls, 374.
Acridine dyestuffs, 318; orange, 319.
Acrolein, 224, 234; from smouldering candles, 251.
Acrospire, 191.
Adjective dyes, 270; dyestuffs defined, 270.
Aërobic ferments, 190.
"After-chroming," 338.
"Ageing," 330.
"Ageing" of logwood, 324.
Air and gas, Explosive mixture of, 70.
Air condensers for gas making, 62.
Air-gas flame, 70.
Air-slaked lime, 130.
Albite, 141.
Albocarbon light, 73.
Albumin, Application of, in calico-printing, 341.
Alcohol, 215 (see also *Spirit*); Absolute, 217; Absolute, strength O.P., 218; Boiling point of, 218; Denaturing, 218; denaturing, Wood naphtha for, 218; Oil soluble in, 235; Oxidation of, 219; Specific gravity of, 218.
Alcoholic strength, Excise system of, 218.
Alcoholometry, 218.

Alcohols, Higher, 217.
Aldehyde, 219.
Aldehydes, Aromatic, 240.
Ale, Mild, 205; Pot, 211; vinegar, 221.
Algarobilla, 378.
Alizarate, Sodium, 281.
Alizarates, 281.
Alizarin, 296, 334; Artificial, 280; black, 279, 280; blue S. (soluble), 282; Bordeaux, 282; colours, Application of, 338; cyanine, 282; Manufacture of, 281; paste, 281; yellow, 338; yellows, 337.
Alkali, Action of, on wool, 271; Act, Regulation of vitriol making, 15; blue, 290; blues, Application of, 388; Electrolytic preparation of, 51; for glass, 151; lime glass, Analysis of, 157; manufacture, Limestone for, 21; Nitrogen in coal for, 22; Raw materials for, 19; Recovery of, in paper making, 345; Refined, 29; Small coal for, 22; trade standards, 31.
Alkali waste, Analysis of, 32; Mactear process for, 34; Parnell & Simpson's process for, 33; Sulphur recovery from, 32; Treatment of, 32; Use of, in phosphate manufacture, 109.
Alkaline carbonates, Saponification with, 247; water, Effect of, in brewing, 199.
Alkalinity, Indicator for, 275.
Almond cake, 214.
,, oil, 226, 231.
Almonds, Artificial oil of bitter, 241; Oil of bitter, 231, 241; Synthesis of oil of bitter, 241.
Alphanaphthylamine, Claret colour from, 335.
Alum, 424; Ammonia, 426; Basic, 425; Burnt, 426; cake, 425; Chrome, 426; Manufacture of, from clay, 425; Preparation of, 425; stone, Analysis of, 424; Tanning with, 390.
Aluminium acetate, Preparation of, 360; Use of, in dyeing, 330.
Aluminium mordants, 330.
,, resinate as a size for paper, 344.
,, shavings for filtering beer, 204.
,, sulphate, 424, 425; Use of, for sugar recovery, 176; Use of, in dyeing, 330.
Aluminium sulphocyanide as a mordant, 341.
,, thiocyanate, Use of, in dyeing, 330.
Alunite, 424.
Amido-acetophenone, 316.
Amido-azobenzene, Formula for, 273; Preparation of, 314.
Amido-azobenzene dyestuffs, Formation of, 274; naphthalene, 301.
Amidotolunaphthazine, 295.
Ammonia alum, 426.
,, crude, Composition of, 47.
,, Fixed, 47; in gas liquor, 75.
,, Free, 47; in gas liquor, 75.
,, from bone distillation, 105; in coal gas, 68; in London gas, Statutory limit for, 74; in soot, 112.
,, Production of, 47; Recovery of, 47.
,, soda ash, Apparent density of, 47.
,, soda process, 43; Carbon dioxide in exit gas from, 46; Reactions in, 43; Recovery of chlorine in, 49; Salt wasted in, 46.
,, "still," 47.
,, Yield of, from gas coals, 75; from Simon-Carvès oven, 87.
Ammoniacal liquor from shale distillation, 102.
Ammoniacal liquor, Valuation of, 76; Yield of, from coal, 66.
Ammonium chromate, 359.
,, orthosulphamidobenzoate, 420.
,, sulphate, as manure, 112; commercial, Impurities in, 112; Manufacture of, 76.
Amygdalin, 241.
Amyl acetate, 217.
,, alcohol, 211; Active, 217; Inactive, 217.
Amylan, 192.
Anaërobic ferments, 190.
Analyser, 212.
Analysis of alkali waste, 32; alum stone, 424; animal charcoal, 104; ash of yeast, 201; barley, 192; basic slag, 110; beet molasses, 173; black ash, 27; bone, 103; brass, 205; brick clay, 145; brine, 20;

Brunswick green, 358; caustic liquor, 31; cement clinker, 139; cement slurry, 138; chalks, 127; charbon roux, 92; charcoal for gunpowder, 401; coal gas, 69; cochineal carmine, 365; cognac, 210; coke, 83; commercial sodium nitrate, 113; cotton fibre, 260; crude nitrate of soda, 112; diastase, 193; distillers' grains, 210; extracts for tanning, 381; fire clay, 145; flax, 261; fortified wines, 208; fusel oil, 217; gas liquor, 75; glass, 157; grape juice, 205; grey chalk, 127; hemp, 261; hides, 370; hydraulic limestone, 126; jute, 262; leather, 392; limestone, 126; magnesian limestone, 126; malt, 192; materials for Portland cement, 138; molasses, 164; native phosphates, 108; natural gas, 118; osseine, 105; Oxford ochre, 364; phosphatic gypsum, 409; Portland cement, 138; products of cane sugar fermentation, 201; puzzuolana, 140; raw silk, 259; rock salt, 19; Roman cement, 133; smalt, 357; soda ash, 29; sole leather, 392; spent beet, 167; spirit, 216; starch-yielding materials, 183; sublimed white lead, 352; sugar cane juice, 163; tank liquor, 28; tanning materials, 379; tanstuffs, 379; treacle, 164; ultramarine, 356; water for brewing, 195; white chalk, 127; wines, 207; wood gas, 95; wool fibre, 258; wort, 98; yeast, 200.
Angelica root, 214.
Anhydrite, 426.
Anhydro-orthosulphamidobenzoic acid, 420; sulphuric acid, 18.
Anilidophenylnaphthinduline, 315.
Aniline black, 311; Dyeing with, 311; "Greening" of, 312; Printing with, 311.
Aniline blues, 290.
,, colours, 287.
,, Dimethyl, 289.
,, dyes, 284.
,, dyestuffs, blue, 289.
,, for blue, 286; for blue, Application of, 290; for red, 286.
,, hydrochloride, 286.
,, Manufacture of, 285.
,, Methylation of, 289.
,, oil, 286.
,, salt, 286.
Aniline violet, 289.
Animal charcoal (see *Charcoal, Animal*).
,, fibres, distinguished from vegetable fibres, 259.
,, oil, 104.
,, oils, Winning and refining of, 229.
Anisidine, 335.
Annaline as a loading material, 344.
Annealing glass, 156.
Antheraea mylitta, 259.
Anthracene, Boiling point of, 82; brown, 338; Conversion of, into anthraquinone, 280; from Russian petroleum, 123; green, 296; Melting point of, 82; oil, 81; Orientation of, 279; Purification of, 82, 280; "Thirty per cent.," 82.
Anthraquinone, Conversion of, into alizarin, 281; Formula for, 279; Manufacture of, 280; Purification of, 281; Sulphonation of, 281; sulphonic acids, 281.
Antimoniate, Lead, 361.
Antimony fluoride, Use of, in dyeing, 332.
Antimony, Golden sulphide of, 244; lactate, 408; potassium oxalate, 417; potassium oxalate, Use of, in dyeing, 332; salts, Use of, in dyeing, 332; vermilion, 363.
Antiseptic, Hydrofluoric acid as an, 413.
Antiseptics, Effect of, on diastase, 193; for beer, 204; for vines, 206.
Apatite, 106.
Apocynaceæ, 243.
Aposafranine, 313.
Aqua fortis, 11.
Arachidate, Glyceryl, 231.
Arachidic acid, 223.
Arachis hypogæa, 231.
Arachis oil, 231.
Archil, Preparation of, 327.
Argand burner, 70.
Argol, 207, 418.
Armstrong's theory of colour, 278.
Aromatic aldehydes, 240.
Arrowroot starch, 183, 187.
Arsenate of soda, Application of, in calico-printing, 341.
"Arsenic," 415.
Arsenic acid, 415; as an oxidant, 287; Manufacture of, from white arsenic, 416; Uses of, 416.
Arsenic glass, 416.
,, in sulphuric acid, 16.
,, kips, 372.

Arsenic, Recovery of, 287; Red, 383; soot, 415.
Arsenic sulphide, 361; as a depilatory, 383.
Arsenic, Vitreous, 416.
Arsenic, White, 415; for curing hides, 372; Purification of, 416; Uses of, 416.
Arsenic, Yellow, 383.
Arsenious acid, 415; anhydride, 415.
Arsenite, Cupric, 359.
Artocarpaceæ, 243.
Asbestos, 262; fabrics, Effect of heat on, 263.
Ascension pipe, 62.
Ascospores, 200.
Ash of yeast, Analysis of, 201.
Asparagine in beet juice, 165.
"Asphalt," 82.
Asphalt cement, 125.
,, mastic, 125.
,, rock, 125.
,, substitute, 253.
Asphaltum, 124; Trinidad, 124.
Assimilation of nitrogen from air, 114; of phosphate manures, Rate of, 111.
Astatki as fuel, 122.
Astralene, 122.
Attemperators, 199.
"Attenuation" of wort, 199.
Auramine, 309, 334.
Aurantia, 273, 336.
Aureolin, 361.
Aurine, 292; dyestuffs, 291.
Autoclave, 253.
Auxochrome, 273.
"Available oxygen" in manganese, 35.
Aventurin, 158; Chrome, 159.
Axle grease, 236.
Azine compounds, 297.
,, Diphenylene, 297.
Azo-benzene, Formula for, 273; diazo-chloride, Formation of, 276.
Azo-blue, 333.
Azo-colours converted into mordant dyestuffs, 337.
Azo-compounds (dyestuffs), 273; explained, 275.
Azo-diphenyl blue, 314.
Azo-dyes, Bleaching of, 278; dyestuffs, Application of, 337.
Azonium bases, 299.
Azophenine, 315.
Azophor red P N, 335.

B

Bacillus viscosus, 204.
Backs, 134.
Bacteria, 189; in yeast, 202.
Bacterium aceti, 219.
Bagasse, 163.
Ball clay, 149.
Ball mill, 111.
Balsam, Peru, 242.
Balsams, 240, 242.
Baltic linseed oil, 234.
Barium chloride, 430.
,, chromate, 361.
,, nitrate in explosives, 405.
,, salts, 430.
,, sulphate, 353.
,, ,, as a loading material, 344.
Bark, Oak, 376; Hemlock, 378.
Barkometer degrees, 388.
Barley, Analysis of, 192; Carbohydrates of, 192; couch, 190; Drying malted, 191; Flooring, 190; "Mealiness" of malted, 191; Necessity for drying malted, 191; Proximate composition of, 192; Steeping, 190; Unsound, as fodder, 190.
Barley for brewing, Character of, 192; for malting, 192; for malting, Character of, 190.
Barwood, 325.
Baryta used for sugar recovery, 176.
Barytes, 353; in white lead, 352.
Base, Primuline, 277.
Basic alum, 425.
Basic colours, Dyeing cotton with, 334; Dyeing silk with, 338; Examples of, 334; "Topping" with, 334.
Basic copper acetate, 359.
,, ,, carbonates, 360.
,, dyes, 330.
,, dyestuffs, Bottoms for, 332.
,, lead acetate, 350.
,, ,, carbonate, 349.
,, ,, chloride, 351.
,, ,, chromate, 361.
,, ,, chromate, Dyeing with, 328.
,, mordants, 330.
,, slag, 110 (see also *Slag, Basic*).
Bassorah galls, 374.
Bast fibres, 260, 262.
Bate, 384; substitutes, 385.
Bating skins, 384.
Batswing burner, 70.
Battery of cells for sugar diffusion process, 166.
"Bay salt," 20.
Bazils, 359.
Beale's rotatory exhauster, 62.
Beard of valonia, 377.
Beckton coal tar, Composition of, 77.

Beech shavings for clarifying wine, 220; for vinegar process, 220.
Beef tallow, 228, 236.
Beehive coke oven, 84.
Beer, Aluminium shavings for filtering, 204; Antiseptics for, 204; Bitter, 205; Caramel for colouring, 182; Cleansing system, 203; Colouring, 204; defined, 190; Diseases of, 204; Finings for, 204; Finishing, 204; Lager, 200; Liquid carbon dioxide for preserving, 204; Pilsener lager, 205; Priming, 204; Racking, 204; Raw materials for, 190; Ropy fermentation of, 204; Sour, 204; "Stench of," 194.
Beeswax, 239; Adulterations of, 239; Bleaching of, 239.
Beet, Analysis of spent, 167; Composition of juice of, 165; Concentration of juice of, 167; Defecation of juice of, 167; Fusel oil from, 217; Yield of juice from, 165; Yield of sugar from, 172.
Beet juice, 165; Purification of, by lime, 167; Trimethylamine from, 165.
Beet molasses, 172; Analysis of, 173; Utilisation of, 173, 176.
Beet sugar (see *Sugar*, *Beet*).
Beilby & Young retort, 97, 99.
Bengal ordinary saltpetre, 400.
Benzal chloride, 241.
Benzaldehyde, 231, 241; green, 291.
Benzene, Boiling point of, 79; Enriching gas by, 73; Induline, 312; Melting point of, 79; Nitration of, 284.
Benzeneazobenzeneazophenol, Formation of, 276; Formula for, 276.
Benzeneazobenzeneazo - β - naphthol sodium disulphonate, 276.
Benzeneazo - β - naphthol sulphonic acid, Formula for, 275.
Benzeneazophenol, Formation of, 274; Formula for, 274.
Benzidine, 277; dyestuffs, 277.
Benzine from petroleum, 120; from shale, 101.
Benzoazurin, 333.
Benzochrome black, 333.
Benzoflavine, 319, 334.
Benzoic acid, 242, 419; Application of, 290.
Benzoin, Gum, 242; Styrax, 242.
Benzol, "Fifty per cent.," 79; Fractionation of crude, 78; from Russian petroleum, 123; "Ninety per cent.," 79; still, Dephlegmator for, 78.
Benzolene, 101.
Benzopurpurin, 333.
Berlin porcelain, 147.
Betaine in beet juice, 165.
Beta vulgaris, 163.
Bicarbonate of soda, 30; Conversion of, into soda ash, 46.
Bichromate, Chrome-alum converted into, 280; Sodium, 421; Potassium, 421; Preparation of, by electrolysis, 422.
Bichromates, 420; as mordants, 331; Recovery of, 280.
Biebrich scarlet, 276.
Bird lime, 239.
Bi-rotation, 181.
"Biscuit firing," 146.
,, porcelain, 149.
Bistre, 328.
Bismarck brown, 275, 334.
Bisulphide of carbon, 436 (see *Carbon bisulphide*).
Bisulphite, Calcium, 6; for making wood pulp, 347.
Bisulphite compounds (dyestuffs), 279.
,, Magnesium, for making wood pulp, 347.
,, Sodium, 6.
Bisulphites, as antiseptics for beer, 204; Manufacture of, 6, 347.
Bitartrate of potash, 418; Use of, in dyeing, 330.
Bitter almonds, Oil of, 231, 241; Artificial, 241; Synthesis of oil of, 241.
Bitter beer, 205.
,, principles for brewing, 194.
Bittern, 21.
Black ash, Analysis of, 27; furnace, 25; Lixiviation of, 27; Manufacture of, 25; process, Reactions in, 25, 26; revolver, 26.
Black beer, Water for, 195.
,, liquor, 95.
,, pigments, 364.
,, salt, 29.
,, sulphur, 355.
,, "tar," 101.
,, vitriol, 424.
Blacks, Diazo, 333.
"Bladder lard," 237.
Blanc fixe, 365; as a loading material, 344.
Blast furnace slag for cement, 140.
Blasting gelatine, 407 (see *Gelatine*, *Blasting*).
Bleach, 51; Electrolytic, Preparation of, 51.

Bleaching, 263; by bleaching powder, 266; by chloride of lime, 266; by hydrogen peroxide, 264, 265; by oxidation, 264; by potassium permanganate, 267; by reduction, 264; by sodium peroxide, 265; by sulphites, 264; by sulphur dioxide, 264; Electrolytic, 267.
Bleaching powder, chambers, 41; Manufacture of, 34; Production of, 40.
Blende, Sulphur dioxide from, 5.
Blind roasters, 23.
Block gambier, 378.
,, kieserite, 427.
,, printing, 340.
Blood albumin, Application of, in calico-printing, 341.
Blood, Defecation of sugar by, 178; Dried, as manure, 113.
Bloom deposited by tannins, 376.
Blown oils, 234.
,, rape oil, 234.
Blubber of whale, 238.
Blue, Aniline, dyestuffs, 289.
Blue bricks, 145.
,, from anisidine, 335.
,, lias limestone, 132 (see *Limestone*.
,, oil, 101.
,, pigments, 354.
,, stone, 423.
,, sulphur, 355.
,, vitriol, 423.
Blues, alkali, Application of, 338; Aniline, 290.
Body of pigments, 348.
Boiled-off liquor, 265; silk, 265.
Boiled linseed oil, 234 (see also *Linseed oil*).
,, oil, 223.
Boiling and mashing, Influence of water used for, in brewing, 199.
"Bombonnes," 24.
Bombyx mori, 259.
Bone, Analysis of, 103.
Bone-ash, 111; superphosphate from, 111.
Bone black, 365.
,, charcoal, 104.
,, distillation, Ammonia from, 105; Gas from, 105.
,, fat, 228; an adulterant of tallow, 237; Recovery of, 103.
,, flour, 111.
,, meal, 111.
,, oil, 104, 227; Specific gravity of, 105.
Bones, Destructive distillation of, 103; Dissolved, 111; for manure, 111; Glue made from, 397; Nitrogen in, 111.
Boracic acid (see *Boric acid*).
Boracite, 426; Stassfurt, 414; Turkish, 414.
Borate, Chromium, 359; glass, 160; Manganous, as a drier, 234.
Borax, 415; Californian, 414; crude, Composition of, 415; Prismatic, 415; Octahedral, 415.
Boric acid, 414; as a preservative, 414; Tuscany, 414; Uses of, 414; Winning of, 414.
Boric anhydride, 414.
Boronatro-calcite, 414.
Bot marks, Prevention of, 372.
Bottle nose oil, 228.
"Bottom acid," 14.
,, fermentation, 200 (see also *Fermentation*).
,, yeast, 202.
Bottoms for basic dyestuffs, 332.
Bouquet of wine, 207, 208.
Boutmy-Faucher method of nitrating glycerine, 405.
"B. O. V.," 15.
Bowk, Lime, 266.
Bran drench, 385; Acids in, 386.
Brandy, 209; Brown, 210; Colour of, 210; Grape, 209; Marc, Fusel oil from, 217; Yield of, from wine, 209.
Brass, Analysis of, 205.
Brassica campestris, 232.
Brazil wood, 325, 334; Colours produced by, 325.
Brazilein, 325.
Brazilian yellow wood, 325.
Brazilin, 325.
Breaking flax, 261.
,, hides, 382.
" ,, the grain," 253.
Breeze, Charcoal, 89.
Bremen blue, 358.
Brewers' grains, 197.
Brewing and distilling, 189; Bitter principles for, 194; Boiling wort in, 197; Character of barley for, 192; Coolers used in, 198; Cooling wort in, 198; Effect of alkaline water in, 199; Effect of sodium chloride in water for, 199; Influence of water on mashing and boiling in, 199; Proportion of yeast used in, 199; Refrigerators used in, 198; Starches for, 193; Sugars for, 193; Water for, 194;

water for, Analysis of, 195; Waters rendered fit for, 195.
Bricks, Blue, 145; Burning of, 145; clay for, Analysis of, 145; Colour of, 145; Fire, 145; Glazed, 145.
Brilliant green, 334.
,, scarlet, 363.
Brimstone, Roll, 2.
Brine, Analysis of, 20; Boiling point of saturated, 20; Pumping, 19; Saturated, for ammonia soda process, 43.
British gum, 187; Manufacture of, 188; Uses of, 188.
Brix degrees, 169.
"Broken baths," 339.
Bromination, Method of, 295.
Bromine absorption, 225.
Bromine, Application of, 295; Extraction of, 431; Impurities in, 431; Purification of, 431; "Solidified," 431; Uses of, 431.
Brown acetate of lime, 93, 95.
,, oil of vitriol, 15.
,, sugar of lead, 95.
,, vegetable colouring matters, 326.
Broxburn shale, Yield of products from, 97.
Brunswick black, 105.
,, green, 358.
,, ,, Analysis of, 358.
Buff, Iron, 328.
Buffs, 391.
Burners, 70; Efficiency of different gas, 71; Illuminating effect of gas burnt in different, 70; Typical gas, 69.
Burning naphtha, 79.
,, oil from petroleum refining, 121.
Burton water, 195.
Burtonising water, 195.
Butane, 120.
Butter, 237; Casein in, 237; Cocoa, 227; Composition of, 237; defined, 237; fat, 228; fat, Properties of, 238; rancid, Butyric acid in, 237; substitute, 238.
Buttery oils, 236.
Butt of hides, 384.
"Butts," 371.
Butyl alcohol, 217.
Butyric acid, 223; in rancid butter, 237.

C

Cadmium sulphide, 361.
Cadmium yellow, 361.
Cæsalpinia, 325; *brevifolia*, 378; *coriaria*, 378.
Cakes, Oil, 233.
Calamus root, 214.
Calcarone, 1.
Calcium bisulphite, 6; for making wood pulp, 347.
,, carbide, 73.
,, carbonate, Dissociation of, 127; Heat of formation of, 127.
,, chlorate, 42.
,, chloride, Function of, in Weldon process, 38.
,, citrate, 419.
,, manganite, 37.
,, monosaccharate, 167.
,, oxalate, 417.
,, saccharate, 167.
,, sulphate, 131; as a loading material, 344.
,, tartrate, 418.
,, thiosulphate, 363.
Calcutta linseed oil, 234.
Caledonian white lead, 353.
Calendering, 345.
Calf-kid, 390.
Caliche, 112; Extraction of iodine from, 432.
Calico-printing, 340; styles of, 340, 341, 342; Thickening agents for, 340.
Californian borax, 414.
Camomile, a hop substitute, 194.
Camphor, 241.
Camphors, 241.
Camwood, 325.
Canaigre, 378.
Candle moulds, 251.
Candle power of cannel gas, 71; coal gas, 68; coal gas determined, 67; oil gas, 74, 75.
Candle, Standard, 67.
,, wick, Function of, 250.
,, wicks, Treatment of, 251.
Candles, 250; Moulded, 251; Ozokerite, 252; Paraffin, 251; Poured, 251; Raw materials for, 250; Sperm, 252; Stearin for, 252; Stearin (stearic acid), 255; Wax for, 251.
Cane sugar, 162, 163 (see also *Sugar, Cane*); Fermentation of, 201; juice (see also *Sugar-cane juice*).
Cannabis sativa, 261.
Cannel, Composition of, 57; for enriching gas, 71; gas, Candle power of, 71; Tar from, 71.

Caoutchene, 243.
Caoutchouc, 243; Behaviour of, when heated, 243; Ceara, 243; Para, 243; Solvents for, 243; Vulcanised, 243.
Caput mortuum, 18.
Caramel, 181; for colouring beer, 182, 204; for colouring sherry, 208; for colouring spirits, 182; for colouring vinegar, 182; made from starch sugar, 182.
Carbide, Calcium, 73.
Carbohydrates, 162; of barley, 192.
Carbolate, Sodium, 79.
Carbolic acid, 79, 80; Specific gravity of crude, 80.
Carbolic oils, 79.
Carbon bisulphide, 436; Boiling point of, 436; Heat of formation of, 436; Plant for making, 436; Removal of, from coal gas, 65; Specific gravity of, 436.
Carbon black, 119, 364.
,, density, 69.
Carbon dioxide from breweries, 205; in exit gases from ammonia-soda process, 46; in lime kiln gases, 46; Liquid, for preserving beer, 204.
Carbon, Gas, 61; Retort, 61.
Carbon tetrachloride, 230, 436; Boiling point of, 436; Specific gravity of, 436.
"Carbonate vessel," 65.
Carbonates, alkaline, Saponification with, 247.
Carbonating tower for ammonia-soda process, 44.
Carbonation of tank liquor, 28.
Carbonic acid from breweries, 205.
Carbonising in retorts for gas production, 58; wood in kilns, 90; wood in retorts, 90.
Carbonyl chloride, Application of, 289, 309.
Carburine, Enriching gas by, 73.
Cardamoms, 214.
Carmin, 327
Carmine, 328; Cochineal, 365.
Carminic acid, 327; Alumina lake of, 328.
Carnallite, 114, 426.
Carriers, Oxygen, 288, 289, 311.
Carthamin, 326.
Carthamus tinctorius, 326.
Casein in butter, 237.
Cassava, 187.
Cassel yellow, 361.
Cassia, 214.
Cast-iron vessels, Concentration of vitriol in, 16.
Castor oil, 227, 235; Action of sulphuric acid on, 235; group, Oils of, 227; Properties of, 235; Refining of, 235; Viscosity of, 235; Yield of, 235.
Catechu, 326, 377.
Caustic ash, 29.
,, liquor, Analysis of, 31.
,, potash, 427.
,, soda, 30 (see also *Soda*).
Causticising process, 30.
,, soda ash by fusion with ferric oxide, 47.
Ceara, caoutchouc, 243; rubber, 243.
Cedar oil, 241.
Cedrene, 241.
Cedrenes, 240.
Celestine blue, 337.
Cells, Battery of, for sugar diffusion process, 166.
Celluloid, Solvent for, 217.
Cellulose, Destructive distillation of, 56; for paper-making, 344; hexanitrate, 403; nitrated, Varnishes from, 246; Nitration of, 404; Nitro-, 403.
Cement, Asphalt, 125; burning, Chemistry of, 138.
Cement, clinker, Constitution of, 139; "Fallen," 139; Proximate analysis of, 139; Under-burnt, 139.
Cement, Effect of temperature on setting of, 131; for china, 397; Grinding, 137; Hydraulic, 132; kilns, 135.
Cement, Portland, 134; Analysis of materials for, 138; clay for, Analysis of, 138; Hardening of, 139; Materials for semi-dry process of mixing, 134; Materials for wet process of mixing, 134; Setting of, 139.
Cement, Puzzuolanic, 140; Roman, Analysis of, 133; Scott's 132; Slag, 141; slurry, Analysis of, 138.
Centrifugal machine, 164.
Ceresin, 124, 413.
Cerotate, Ceryl, 228; Myricyl, 228.
Cerotic acid, 223, 239.
Ceryl cerotate, 228.
Cetyl palmitate, 228, 239.
Chalk, Analysis of grey, 127; Analysis of white, 127; Levigated, 353.
Chamber acid, 14; specific gravity of, 14.
,, crystals, 12; method of making white lead, 350.

Chamois leather, 391.
Champagne, 208.
Chance-Claus process, 32.
Charbon roux, Analysis of, 92.
Charcoal, Absorption of gases by, 92; Analysis of animal, 104.
Charcoal, animal, Use of, in oil refining, 229; in sugar refining, 178.
Charcoal, Bone, 104; breeze, 89; burning in heaps, 88; in meilers, 88.
Charcoal for gunpowder, 401; Analysis of, 401.
Charcoal from straw, 402; Specific gravity of, 89; Wood, for purifying spirit, 216; Yield of, from wood, 89, 90.
"Char," 104.
Char for sugar refining, 178.
Char, Reburning, 179; Revivified, 179.
"Char-water," 178.
"Check vessel," 65.
Chemicking, 266.
Chili saltpetre, Perchlorate in, 432.
Chimney gases, Hydrochloric acid in, 24.
China, Cement for, 397; clay as a loading material, 344; grass, 262; grass, Bleaching, 267; stone, 148.
Chinese blue, 353.
,, galls, 374.
,, process for making vermilion, 362.
,, wood oil, 227.
Chlorates, 42; Electrolytic preparation of, 51.
Chloride, Benzal, 241; of lime, Bleaching by, 266; of lime, Production of, 41.
Chlorination, Mordanting by, 264.
Chlorine, Liquid, 42; Boiling point of, 42; Specific gravity of, 38.
Chlorine, Manufacture of, 35; Manufacturing yield of, 37.
Chlorine process, Deacon's, 39.
Chlorine, Recovery of, by Weldon-Péchiney process, 50; in ammonia-soda process, 49; process, Mond's, 50.
Chlorine stills, 35.
Chlorosulphite of lead, 353.
Cholesterol, 228, 258.
Choline in hops, 194.
Chondrin, 396.
Chromate, Ammonium, 359; Barium, 361; Basic lead, 361; Lead, 360; Mercurous, 359; Sodium, 421; Stannic, as pigment for glass, 160; Zinc, 361.
Chromates, 420; Manufacture of, from chrome iron ore, 420.
Chrome, alum, 426; alum converted into bichromate, 280.
,, aventurin, 159.
,, brown, 337.
,, green, 359.
,, iron ore, 420; Manufacture of chromates from, 420.
,, orange, 360.
,, red, 337.
,, tanning, 390.
,, yellow, 337, 360; "pure," 361.
Chromic acetate, Use of, in dyeing, 331.
Chromic acid, 422; as a mordant, 331; for purifying spirit, 216; for wax bleaching, 239.
Chromic anhydride, 422.
,, fluoride, Use of, in dyeing, 331.
,, oxide, 359.
,, sulphate, Use of, in dyeing, 331.
,, thiocyanate, Use of, in dyeing, 331.
Chromite, 420.
Chromium acetate as a mordant, 341.
,, borate, 359.
,, fluoride as a mordant, 338.
,, greens, 359.
,, mordants, 331.
,, phosphate, 359.
Chromogen, 273; I., Application of, 338.
Chromophore, 273.
Chromotropic acid, 338.
Chromotrops, 337.
Chrysamine, 336.
Chrysaniline, 287; Manufacture of, 318.
Chrysoidine, 274, 334.
Chrysophenin, 333.
Cider, Composition of, 209; vinegar, 221.
Cinnamic acid, 242.
Cinnamon, 214.
Citrate, Calcium, 419.
Citric acid, 418; as a resist, 342.
Claret, 207.
Clarifying wine, Beech shavings for, 220.
Claus kiln, 33.
Clay, 143; Analysis of, 143; of brick, 145; of fire, 145; China, as a loading material, 341; Cornish, 144; for Portland cement,

Analysis of, 138; Gault, 134; industries, 143; Manufacture of alum from, 425; marls, 144; Plastic, 144; Porcelain, 144.
Clays, Classification of, 144; Fire, 144; Fusibility related to composition of, 144; Plasticity related to composition of, 144; pottery, Analysis of, 143; pottery, Properties of, 143.
Clean spirit, 211.
Cleansing and softening hides, 381.
,, beer, Systems of, 203.
,, fibres, Principles of, 263.
Clichy process for making white lead, 351.
Clinker Cement, 139.
Close test, Flashing point, 121.
Close woods (dyewoods), 325.
Cloth brown, 337.
,, red, 337.
Coal, Destructive distillation of, 56.
Coal distillation, Distribution of nitrogen in, 61; Influence of temperature of, 60; Lime used in, 61.
Coal, Energy value of gaseous products from, 73; for alkali manufacture, Nitrogen in, 22; Small, for alkali manufacture, 22; Valuation of, for gas making, 57; Yield of ammoniacal liquor from, 66; of coke from, 66; of gas from, 66; of tar from, 66.
Coal gas, Action of lime purifier on, 65; Ammonia in, 68; Amount of impurities in crude, 66; Analysis of, 69; Candle power of, 69; Composition of, 66; Determination of sulphur compounds in, 68; Diluents in, 69; Enrichment of, 71; Enriching, by oil water gas, 72; Ferric oxide purifier for, 64; Illuminants in, 69; Illuminating power of, 69; Influence of temperature of distillation on, 67; Non-illuminant combustible gases in, 69; Removal of carbon bisulphide from, 65; "roughed," 64; Standard limits for impurities in, 68; Sulphur compounds in, 68; Sulphuretted hydrogen in, 68; Valuation of, 67.
Coals, Composition of gas, 57; gas, Influence of composition of, on yield of coke and gas, 57; Yield of ammonia from gas, 75; Yield of coke from gas, 60; Yield of gas from gas, 60; Yield of tar by different, 76.
Coal tar, 76; Composition of Beckton, 77; Constituents of, 76; Crude naphtha from, 78; Distillation of, 77; First runnings from, 78; Light oil from, 78; Pitch, 82; Products from distillation of, 77; Quinoline from, 317; Specific gravity of, 76.
Coal washing, 83.
Cobalt blue, 358.
,, glass, 159.
,, yellow, 361.
Coccerin, 327.
Cocceryl coccerate, 327.
Coccus cacti, 327.
,, *ilicis*, 328.
,, *lacca*, 242.
Cochineal, 327; Artificial silver grain on, 327; black, 327; carmine, 365; carmine, Analysis of, 365; Granilla, 327; Silver grain, 327.
Cocoa butter, 227.
,, gunpowder, 402.
Coco-nut cake as fodder, 236.
Coco-nut oil, 227, 236; deflavoured, 238; for margarine, 238; night lights, 251; Properties of, 236; Refining of, 236; Yield of, 236.
Cocos nucifera, 236.
Cod-liver oil, 228, 238; Adulterations of, 239; Medicinal, 238; Properties of, 238; Tanner's, 238.
Cœlestine, 429.
Cœruleïn, 296, 334, 338.
Coffey still, 212, 213.
Cognac, 209; Analysis of, 210.
Coke, Analysis of, 83.
Coke from petroleum distillation, 83; Gas, 82.
Coke oven, 83; Beehive, 84; Coppée, 87; Simon-Carvès, 86.
Coke, Yield of, from coal, 60, 66; from Simon-Carvès oven, 87.
Coking in heaps, 83; in modern ovens, 85; with recovery of products, 85.
Colcothar, 18, 363.
Cold drawn oil, 229.
,, press, Oil from, 229.
Colinin, 325.
Collagen, 369.
Colloidal character of starch, 187.
Colophony, 241.
Colour, Armstrong's theory of, 278; correctives, 152, 187, 353.
Colour lakes, 330.
,, of mixed pigments, 348.
,, printing, 340.
Colouring matters, 273; Mineral, 328.

Colours, Aniline, 287; Developers for, 333; Fast, defined, 270; Ingrain, 277, 335.
Column still, 212.
Colza oil, 232.
"Cooler grounds," 198.
Coolers used in brewing, 198.
Combustion tube glass, Reason for refractory character of, 157.
Condenser, Air, for gas making, 62; Guttmann's nitric acid, 10.
Cones, Seger's, Temperature measured by, 147.
Confectionery flavourings, 217, 241.
Congo red, 277, 333.
Coniferine in beet juice, 165.
Conifers, a source of turpentine, 240.
Coniine, 105.
Connective tissue, 368.
Copal, 242.
Cop-dyeing, 329.
Coppée coke oven, 87.
Copper, Action of acetylene on, 74.
Copper acetate, Basic, 359.
,, acetoarsenite, 359.
,, carbonate, Basic, 360.
,, oxychloride, 358.
,, sulphate, Manufacture of, 427; Uses of, 423.
Copperas, 423; vat for dyeing with indigo, 322.
Coprah, 236.
Coprolites, 107.
Coralline yellow, 292.
Corchorus, 262.
Cordite, 407
Coriander, 214.
Coriin, 369.
Corium, 367.
Cornish clay, 144; stone, 149.
Correctives of colour for glass, 152.
Cosettes, 165.
Cotton, 260; Action of acids and alkalies on, 260; bleaching, 265; dyeing, 333, 334.
Cotton fibre, 260; Analysis of, 260; Structure of, 260.
Cotton, Flax colder than, 261; Flax compared with, 261; Relation of, to dyestuffs, 272; Scouring, 265; Scouring, Chemistry of, 266; "Staple" of, 260; Yellow colour of bleached, corrected, 267.
Cotton-seed blue, 232; cake as fodder, 232.
Cotton-seed oil, 226, 232; an adulterant of lard, 237; group, Oils of, 226; Properties of, 232; Uses of, 232.
Cotton-seed stearin, 232; an adulterant of tallow, 237.
Cotton singeing, 265; wool, 260.
Couch, Barley, 190.
Covering power of mixed pigments, 348.
"Cracking" of hydrocarbons in gas making, 61; petroleum, 119.
"Craze," 149.
Cream of tartar, Use of, in dyeing, 330.
Cream separated from milk, 237.
Creolin, 79.
Creosol, 93.
Creosote for lighting, Use of, 81; oils, 80; Wood tar, 93.
Cresotinic acid, 385.
Cresylic acid, 79.
Crimson lakes, 328.
Crocein orange, 275; scarlet, 276.
Croton oil, 227.
Cruciferæ, Oils of the, 226.
Crust, 289.
Crust of wine, 208.
Crutch pan, 249.
Cryolite, Carbonate of, sodium prepared from, 51.
Crystal carbonate, 29; tannin, 375; violet, 289.
Crystallisation of salts with each other, 423.
Cube sugar, 180; gambier, 378.
Cullet, 152.
Cupric arsenite, 359.
Curcas oil, 227.
Curcuma tinctoria, 326.
Curcumin, 326.
Curd soap, 248.
Curried leather, 389.
Currying leather, 393; Oils used in, 393.
"Curtains" of vitriol chambers, 7.
Cutch, 326, 377.
Cuttle fish secretion, 365.
Cyanamine, 308.
Cyanide, Potassium, 434.
Cyanides prepared from gas purifier, 433; Production of, 433.
Cyanine, 317, 338; Iso-amyl, 317.
Cyanines, 316.
Cyanogen compounds, 432; Formation of, from carbon and nitrogen, 432; Heat of formation of, 432.
Cylinder oils, 123.
Cymene, 240.
Cymogene, 120.

D.

Deacon's chlorine process, 39.
Dead-burnt lime, 120.
Deblooming mineral oils, 122.
„ oils, Nitronaphthalene for, 81.
Decortication, 232; of seeds, 229.
Defecation of juice of beet, 167; of sugar by blood, 178.
Dégras, 391, 393; former, 393.
Degreasing skins, 383.
Demerara sugar, 177; Tin in, 180.
Denatured spirit for varnishes, 219.
Denaturing alcohol, 218.
Denaturing spirit, German system of, 219; Oil of turpentine for, 219; Pyridine bases for, 219.
Denitration of artificial silk, 260.
Denitrifying organism, 113.
Dephlegmator for benzol still, 78.
Depilatories, 383.
Desmobacterium hydrogeniferum, 323.
Destructive distillation, Principles of, 55; Typical products of, 56.
Detergent action of soaps, 250; properties of soap enhanced, 247.
Detergents, 417.
Detonation, Explosion contrasted with, 399.
Detonators, 408.
Developers for ingrain colours, 333.
Devitrification of glass, 156.
Dextrin (dextrine), 187; Achroo, 197; Erythro, 197; Malto, 196; Manufacture of, 188; Uses of, 188.
Dextropinene, 240.
Dextrose, Composition of commercial, 182; for sweetmeats, 182; Properties of, 181; Purification of, 182; Sweetening power of, 181.
Diabetic patients, Sugar for, 182.
Dialysis of glycerin, 255.
Diamidoazobenzene, Formation of, 274; Formula for, 274.
Diamidotriphenylmethane dyestuffs, 291.
Diamine black, 333; blue, 333; fast red F, 336; red, 333; yellow, 337.
Diamond black, 119, 364; yellow, 337.
Diastase, 192; Analysis of, 193; Effect of antiseptics on, 193; Isolation of, 193.
Diastatic power of malt, 192; Lintner's standard of, 193.
Diazoamidobenzene, Preparation of, 314.
Diazobenzene chloride, Formula for, 274; Formation of, 274.
Diazo blacks, 333.
Diazo-compounds, 274; defined, 275.
Diazotising, Process of, 274.
Dibdin's standard lamp, 68.
Dicalcium phosphate, 109.
Diethylamidophenolphthalein, 296.
Diethylmetamidophenol, 296.
Dietzsch kilns, 135.
Diffusers for sugar extraction, 166.
Diffusion process for extracting beet sugar, 165.
Digallic acid, 374.
Dihydroxyanthraquinone quinoline, 282.
Dihydroxynaphthoquinone, 279.
Dihydroxyphthalophenone, 293.
Dihydroxytartaric acid, 310.
Dihydroxytoluic acid, Formula for, 327.
Diluents in coal gas, 69.
Dimethylamidoazobenzene sulphonic acid, Formula for, 275.
Dimethylaniline, 289.
Dimethylparaphenylenediamine, 299; Application of, 305; Sulphosulphonic acid, 306.
Dinas fireclay, 144.
Dinitro-α-naphthol, 273.
Dinitro-benzene, Manufacture of, 284.
Dinitrosoresorcinol, 302.
Dinsmore process, 74.
Diphenylene azine, 297.
Diphenylnaphthylmethane dyestuffs, 290.
Dippel's oil, 104.
Dips, Tallow, 251.
Direct colours, Dyeing silk with, 338; dyes, 330; dyestuffs, Examples of, 333.
Disaccharides, 162.
Disazo-compounds defined, 375; dyestuffs, Formation of, 276.
Discharge pastes, Oxidising, 342; Reducing, 341.
Discharge, Stannous acetate as a, 341; style of calico-printing, 341; Zinc dust as a, 341.
"Discharging" silk, 265.
"Diseased" wool, 257.
Diseases of beer, 204.
Di-sodoxyanthraquinone, 281.
Dissociation of calcium carbonate, 127.
Dissolved bones, 111.
Distillation, Destructive, 35.
Distilled oleic acid, 253; verdigris, 360.

Distillers' grains, Analysis of, 210.
Distilling and brewing, 189.
Di-strontium saccharate, 175.
Divi-divi, 278.
Dodecatyl alcohol, 228; oleate, 239; physetoleate, 239.
Dœglic acid, 223, 228.
Dœgling oil, 228.
Dolomite limestone, 126.
"Double superphosphate," 109.
"Draff," 210.
Drawing gas retorts, 60.
Drenching skins, 385.
Dressed leather, 389.
Dressing leather, 389.
Drier for manure manufacture, 409; Litharge as a, 234; Manganese borate as a, 234.
Driers, 234.
Drips, Acid, in vitriol chambers, 14.
Dropping pipe, 212.
Drying oils, 226, 234; defined, 224; Oxidation of, 224; Semi-, 233.
Drysalted hides, 372.
Duncan and Newland's process, 176.
Dung, Application of, in making white lead, 349.
Dust from pyrites burners, 6.
Dutch process for making vermilion, 362; white lead, 349.
Dyeing and mordants, 329; bath, Circumstances influencing constitution of, 329.
Dyeing cotton, 333; with acid colours, 334; with basic colours, 334; with direct dyestuffs, 333; with mordant dyes, 334; with special dyes, 334.
Dyeing, Chemical theory of, 271; Cop-, 329; General principles of, 270; Hank-, 329; ingrain, Advantage of, 277; ingrain, Methods of, 277; Jute, 339; Leather, 393; Methods of, 329; mixed fabrics, 336, 338, 339; Physical theory of, 271; Theory of, 271; tone produced in, Influence of the fibre on, 335; "Vat-," with indigo, 322; Water for, 343; Witt's theory of, 273.
Dyeing silk, 338; with acid colours, 339; with basic colours, 338; with direct colours, 338; with mordant colours, 339.
Dyeing style of calico-printing, 341.
Dyeing with aniline black, 312; with basic lead chromate, 328; with chrome yellow, 328; with cochineal, 327.
Dyeing with indigo, 322; Copperas vat for, 322; Hyposulphite vat for, 323; Wood vat for, 322.
Dyeing with ingrain colours, 333; with lead chromate, 328; with manganese brown, 328; with orange chrome, 328; with Prussian blue, 328.
Dyeing wool with acid colours, 336; with basic colours, 336; with direct dyes, 335; with mordant colours, 337.
Dye, Lac, 242, 328.
Dyes, Acid, 330; Acid, classified, 336; Adjective, 270; Aniline, 284; Basic, 330; Direct, 330; distinguished from dyestuffs, 270; Mineral, 328; Mordant, 330; mordant, Examples of, 334; Special, 330; Substantive, 270; substantive, Examples of, 333.
Dyestuffs, Acridine, 318; Adjective, defined, 270; Application of sulphonic acid, 336; Aurine, 291; Azo, converted into mordant colours, 337; Azo-compounds, 273; blue, Aniline, 289; Classification of, 273; classified according to mode of application, 329; containing sulphur, 304; Diamidotriphenylmethane, 291; Diphenylnaphthylmethane, 290; Disazo, 276; distinguished from dyes, 270; distinguished from pigments, 270; Examples of direct, 333; Formation of amidoazo, 274; Formation of hydroxyazo, 274; from naphthols, 275; Methylation of aniline, 289; Natural organic, 319; Nitrocompounds as, 273; Organic synthetic, 273; Oxazine, 307; Phthalein, 292; Primuline, 277; Quinone derivatives as, 278; Relation of cotton to, 272; Relation of fibres to, 271; Substantive, defined, 270; Trihydroxytriphenylmethane, 291; Triphenylmethane, 283; Tetrazo, 275; tetrazo, Formation of, 276; Violet aniline, 289; Witt's Theory of, 273.
Dyewoods, 325.
Dynamite, 406; Explosion of, 407; Gelatine, 407; Manufacture of, 406.

E

Earthenware, 149; Kilns for, 150.
Earth nut oil, 226, 232; cake, 232;

Detection of, 232; Iodine absorption of, 232; Saponification equivalent of, 232; Specific gravity of, 232; Uses of, 232; Yield of, 232.
East Indian kips, 372; linseed oil, 234.
Eau de Javelle, 41.
,, *Labarraque*, 41.
Ebonite, 244.
E.C. power, 405.
Edge runner, 360.
Egg-yolk, Application of, in tanning, 390.
Elaidin reaction, 226.
Elais guineensis, 236.
Elastic fibres, 370.
Elastin, 370.
Electric furnace for phosphorus manufacture, 410.
Electric tanning, 388.
Electrolysis of magnesium chloride, 267; Preparation of bichromate by, 422.
Electrolytic bleaching, 267.
Electrolytic preparation of alkali, 51; of bleach, 51; of chlorates, 51.
Electrolytic process, Greenwood, 52.
Ellagic acid, 376.
Elution, Sugar recovered from molasses by, 174.
Emerald green, 359.
Emeraldine, 312.
Emulsifying power of lanolin, 258.
Emulsin, 241.
Encaustic tiles, 145.
Endogenous division of yeast, 200.
Energy absorbed in production of water gas, 72; changes in alkali processes, 53; into light, Conversion of, 71; of explosives, 398; value of gaseous products from coal, 73.
Engine oil, Olive oil as, 231.
English galls, 374; soft porcelain, 148; sulphuric acid, 17.
Enriching coal gas by oil water gas, 72.
Enriching gas by acetylene, 74; by benzene, 73; by carburine, 73; by naphthalene, 73; by tar, 74; Cannel for, 71.
Enrichment of coal gas, 71.
Enzymes, 189; Typical effect of, 189.
Eosin scarlet, 295; Soluble, 295.
Eosins, 294.
Epidermis, 367.
Epsom salts, 427.
Equivalents, Mean, of oils ascertained, 225.
Erector muscle, 368.
Erucate, Glyceryl, 232.
Erucic acid, 223, 226.
Erythrin, 327.
Erythro-dextrin, 197.
Erythrosin, 295.
Erythrozyme, 280.
Esparto, 262, 344; boiling, 345; Manufacture of paper from, 345.
Essential oils, 240; Winning of, 241.
Etageofen, 135.
Etching glass, 160.
Ether tannin, 375.
Ethereal salts, 223, 240.
Ethylidene lactic acid, 417.
Euphorbiaceæ, 243.
Eurhodol, 298, 299.
Euxanthic acid, 366.
Evans photometer, 67.
Evaporator, Multiple effect, 170, 346; Triple effect, 170; Wetzel, 164; Yaryan, 170.
Excise system of stating alcoholic strength, 218.
Exhauster, Beale's rotatory, 62.
Exothermic decomposition of wood, 96.
Explosion contrasted with detonation, 399.
Explosive mixture of gas and air, 70.
Explosive, Picric acid as an, 408.
Explosives and matches, 398.
Explosives, Barium nitrate in, 405; defined, 398; Energy of, 398; High, 403; Measurement of effective pressure exerted by, 399; Nitro-, 403; Rapidity of, 399; Sprengel's, 408.
Extractor for use with volatile solvents, 230.
"Extracts" for tanning, 380; Analysis of, 381.

F.

Fabrics, Effect of heat on asbestos, 263.
"Fallen" cement clinker, 139.
Falling of skins, 373.
Farmyard manure, 114.
Fast colours defined, 270.
Fastness of indigo, Cause of, 322.
Fat from omentum of pig, 237.
"Fat" lime, 127, 130.

Fats, 223; Differences of, from waxes, 225; Hydrolysis of, 252; Hydrolysis of, by steam, 253; Hydrolysis of, by sulphuric acid, 253, 224; Identification of, 225; Rendering, 229; Saponification of, 225.
Fats and oils, Classification of, 226; Hydrolysis of, 224; Preparation of, 226; Properties and Uses of, 224, 226, 231; Use of, in soap making, 247.
Fatty acids applied as mordants, 332.
Fatty acids, Formulæ of, 223; Melting point of, 223; Solid, made from oleic acid, 255; Table of, 223; volatile with steam, 227.
"Feeding back," 203.
Feet of cattle, Oil from, 236.
Fehling's solution, 193.
Feints, 211.
Felspar, 143.
Fennel, Sweet, 214.
Ferment, Acetic acid, 219; defined, 189.
Fermentation, Acetic, 219; Analysis of products of cane sugar, 201; Artificial cooling for bottom, 200; Bottom, 200; Bottom of wine, 206; Chemistry of alcoholic, 201; defined, 189; Glycerin produced during, 201.
Fermentation of cane sugar, 201; of grape juice, 206; of milk sugar, 201; of molasses, 215; of must, 206; of sugar, 201; of wine, Effect of plaster of Paris on, 208; of wort, 199; of wort for whiskey, 210.
Fermentation, Refrigerating for bottom, 198; Ropy, of beer, 204; Starch separated from gluten by, 185; Succinic acid produced in acetic, 219; Top, 199; Top, of wine, 206.
Fermenting tuns, 199.
Ferments, Aërobic, 190; Anaërobic, 190; Organised, 189; Organised, classified, 189; Typical effects of, 189; Unorganised, 189.
Ferric chloride as an oxidant, 305.
Ferric oxide, 363; Causticising soda ash by fusion with, 47; purifier for coal gas, 64.
Ferricyanides as oxidants, 342.
Ferricyanide, Potassium, 434.
Ferrite, Sodium, 47.
Ferrocyanide, Potassium, 433, 434.
Ferrous acetate, Use of, in dyeing, 331.
,, chloride as a carrier in reducing nitrobenzene, 285.
,, chromite, 420.
,, sulphate, Manufacture of, 423; Use of, in dyeing, 331; Uses of, 424.
Fibre, Bast, 260, 261, 262.
,, Cotton, 260; Analysis of, 260; Structure of, 260.
,, Flax, 261; Analysis of, 261.
,, Hemp, 261.
,, Silk, 259; Behaviour of, to reagents, 259; Specific gravity of, 259.
,, Wool, Analysis of, 258; Properties of, 259; Specific gravity of, 259.
Fibres, Animal, distinguished from vegetable, 259.
,, Mineral, 262; Relation of, to dyestuffs, 271.
,, Textile, 257; length of, 257.
Fibrin, 192.
Fibroin, 259.
Ficus indica, 242.
"Fifty per cent. benzol," 79.
"Figging" in soft soap, 249.
Filling materials for soap, 247.
Filter press, 168.
Filter, Taylor's, 178.
Filtration, Twill bags for sugar, 178.
Fining beer, Isinglass for, 204.
"Finings" for beer, 204.
Finishing beer, 204; processes in tanning, 392.
Firebricks, 145.
Fireclay, Analysis of, 145; Dinas, 144.
Fireclays, 144.
Firing gas retorts, Percentage of coal needed for, 58.
First jet sugar, 172.
First runnings from coal tar, 78.
Fisetin, 325.
"Fishing salt," 20.
Fish-tail burner, 70.
Fission of yeast, 200.
Fitted soap, 248.
"Fixed ammonia," 47; in gas liquor, 75.
Fixing tannin in leather, 393.
Flame, Air-gas, 70.
Flashed glass, 158.
Flashing point, close test, 121; of kerosene, 121; open test, 121.
"Flare lime," 128.
Flavaniline, 316.

Flavin, 326.
Flavopurpurin, 281.
Flavourings, 241.
Flax, 260; "Breaking," 261; colder than cotton, 261; compared with cotton, 261.
Flax fibre, 261; Analysis of, 261.
Flax, Tensile strength of, 261; "Heckling," 261; "Retted," 260; "Retting," 260; "Rippling," 260; "Scutching," 261; Seed, 223; "Staple" of, 261; Structure of, 261.
Flint glass, 158.
Flooring barley, 190.
Flour, Application of, in tanning, 390; Saltpetre, 400.
"Flowers of madder," 280; of sulphur, 2.
Fluorescein, 293; Preparation of, 294.
Fluoride, Antimony, 332; Chromic, 331; Chromium, as a mordant, 338; Sodium, as an antiseptic for beer, 204.
Fluorindines, 315.
Food, Lard as, 237; Oils for, 231, 232, 233.
Fore-shots, 211.
Forge scale, 158.
Formaldehyde, 370.
Formaline, 370.
Fortified wines, 207.
Foul main, 62.
Fourners burner, 70.
Fractionation of crude benzol, 78; of whiskey, 211.
"Free ammonia," 47; in gas liquor, 75.
Freezing, Concentration of glycerin by, 256; Purification of benzene by, 79.
French process of making white lead, 351.
French turpentine, 240.
Frit, Porcelain, 148.
"Fritting," 148.
Frizz, 382.
Frothing prevented in whiskey stills by soap, 211.
Fruit, Oils won from, 238; sugar, 182.
Fuchsine, 287.
Full bleach, 267.
Fulminate of mercury, 408.
Fungi, 189.
Furfural in brandy, 210.
Fusees, 412.
Fusel oil, 202, 211; Analysis of, 217; Content of, in crude spirit, 216; from beet, 217; from brandy marc, 217; from grain, 217; from potatoes, 217; in whiskey, 211; Removal of, from crude spirit, 216, 217; removed from spirit by oxidation, 216.
Fustet wood, 325.
Fustic, 325.
Fustin, 325.

G

Galactose, 162.
Galena, Lead sulphate manufactured from, 352.
Gall and West-Knight process, 79.
Gallein, 296.
Gallic acid, 375; Application of, 296.
Gallipoli oil, 231.
Gall-nuts, 374.
Gallocyanin, 308.
Galloflavine, 338.
Gallo-tannic acid, 374.
Galls, Acorn, 374; Bassorah, 374; Black, 374; Blue, 374; Chinese, 374; English, 374; Extraction of tannin from, 374; Japanese, 374; Levant, 374; Oak, 374; White, 374.
Gall-tannin, Use in dyeing, 332.
Gambier, 326, 377; Block, 378; Cube, 378.
Gambine, 338; R, 302; Y, 302.
Gamboge, 242.
Gambogic acid, 242.
"Garancin," 280.
Gas, Analysis of natural, 118; of wood, 95.
Gas and air, Explosive mixture of, 70.
Gas and Coke, Influence of composition of gas coals on yield of, 57.
Gas burner, Incandescent, 70.
Gas burners, Typical, 69.
Gas burnt in different burners, Heating effect of, 70; Illuminating effect of, 70.
Gas, Candle power of cannel, 71; of coal, 68; carbon, 61; coals (see *Coals, Gas*); coke, 82; Energy absorbed in production of water, 72; enriching (see *Enriching gas*).
Gas from bone distillation, 105; from coal, Yields of, 66; from shale distillation, 103.
Gas, Generator, 72.
Gas liquor, 75; Analysis of, 75; Fixed ammonia in, 75; Free ammonia in, 75; Recovery of sulphur from, 76; Valuation of, 76.

Gas making, Air condenser for, 62; "Cracking" of hydrocarbons in, 61; Plant for, 62.
Gas, Manufacture of water, 72.
Gas, Oil, 74; Candle power of, 74, 75; "Hydrocarbon" from, 75; Pintsch system for, 74; Yield of, per gallon of oil, 74.
Gas, Oil-water, Composition of, 72; Solar oil for, 72.
Gas producer, 72; for retort furnace, 59.
Gas production, Carbonising in retorts for, 58.
Gas purification, Weldon mud for, 66.
Gas purifiers, 64; Arrangement of, 65.
Gas retort, Dimensions of, 58; furnace, 58.
Gas retorts, Charging, 60; Drawing, 60; Mechanical charging of, 60; Percentage of coal needed for firing, 58; Process of distillation in, 60.
Gas, Statutory limit for ammonia in, in London, 75; supplied to Scotch towns, Composition of, 71.
Gas washer, 64.
Gas, Yield of, from gas coals, 60.
Gaseous products from coal, Energy value of, 73.
Gases, Absorption of, by charcoal, 92; in coal gas, non-illuminant combustible, 69.
Gasolene, 120; from shale distillation, 103.
Gaultheria procumbens, 240.
Gay-Lussac tower, 8; Function of, 13; Sulphuric acid for, 13.
Gelatine, Blasting, 407; Explosion of, 407; Manufacture of, 407; Thermal effect of explosion of, 407.
Gelatine, Characters of, 396; Composition of, 396; Drying, 396; dynamite, 407; glue and size, 395; Manufacture of, 396; Properties of, 370; Ultimate composition of, 369.
Gelatinisation of starch, 187.
Gemmation of yeast, 200.
Gems, Artificial, 158, 159.
General manure, Definition of, 106, 114.
Generator gas, 72.
Gentian, a hop substitute, 194.
German method of making white lead, 350.
German spirit, 215.
Germicides, 423.
Germination, Chemistry of, 192.
Germ of maize removed, 186.
Gin, 212; Content of alcohol in, 215; Flavouring matters for, 214; Plymouth, 215; Sweetened, 214.
Ginger-beer, Composition of, 209.
Ginger-beer plant, 200.
Glass, 150; Action of solutions on, 161; Alkali for, 151; Analysis of alkali lime, 157; Annealing, 156; Arsenic, 416; Black, 159; Blue, 159; Borate, 160; Cobalt, 159; Coloured, 158; Colouring, 158; Colour of corrected, 152; combustion tubing, Reason for refractory character of, 157; Crown, 155; Cut, 158; Devitrification of, 156; etching, 160; etching, Hydrofluoric acid for, 160, 413; Flashed, 158; Flint, 158; Fluorescent, 159; for thermometers, 160; furnace, 153, 154; gall, 152; Green, 159; "Hardening," 156; Highly refractive, 160; Influence of composition on index of refraction of, 161; Influence of composition on specific gravity of, 160; Lead, 157; Lead oxide for, 151; Lime for, 151; Limits of composition of, 150; makers' soap, 152; Manufacture of, 155; Opal, 160; Orange, 159; Oxide of iridium pigment for, 160; Oxide of uranium pigment for, 160; Painting on, 160; Plate, 156; Platinum pigment for, 160; -pot, 152; "Potash," 157; -pot, Lead, 158; Properties of, 160; Raw materials for, 150; Red, 158; Ruby, 159; Selenium, 159; Siemens' toughened, 156; Silica for, 151; "Soda," 157; Sodium sulphate for making, 24; Soluble, 141; Stannic chromate pigment for, 160; stills, Concentration of vitriol in, 15; Thallium, 160; Toughened, 156; Uranium, 159; Use of oxygen in making, 155; vessels rendered resistant by steaming, 161; Violet, 159; Water, 141; wool, 263; Yellow, 159.
Glauber's salt, 427; Use of, in dyeing, 335.
Glazes, Coloured, 148; for earthenware, 149; for porcelain, 147; for stoneware, 149.
Glazing gunpowder, Graphite for, 402.
Glazing, Salt, 149.
Glove-kid, 390.

Glover tower, 7; acid, Specific gravity of, 15; Sodium nitrate in, 14.
Glucosan, 181.
Glucoses, 181.
Glucosides, 241.
Glued materials, Mechanical strength of, 397.
Glue, Manufacture of, 297; Silk, 259.
Glues, Liquid. 397.
Glutamine in beet juice, 165.
Gluten recovered in starch-manufacture, 189.
Gluten, Starch separated from, by caustic soda, 185; Starch separated from, by fermentation, 185.
Glycerides, 223.
Glycerin, 255; Boiling point of, 255; Concentration of, by freezing, 256; Dialysis of, 255; produced during fermentation, 201; Recovery of, 255; Recovery of, from soap lyes, 249; Refining of, 255; Uses of, 256.
Glyceryl, 223; arachidate, 232; erucate, 232; hypogæate, 232; iso-linoleate, 233; laurate, 236; linolate, 233; myristate, 238; oleate, 224, 225, 226, 227, 228, 231, 233, 236, 237; palmitate, 224, 228, 231, 236; physetoleate, 238; ricinoleate, 235; salts, Oils not containing, 228; stearate, 224, 228, 237; sulphuric acid, 253; trinitrate, 405.
Glycocoll, 419.
Golden sulphide of antimony, 244.
Gold-lined stills for vitriol, 16.
Gossypium, 232, 260.
"Gradation towers," 21.
Grain of leather, 368; Artificial, 393.
Grain, Fusel oil from, 217.
Graining hides, 389.
Grain-lac, 242.
Grains, Analysis of distillers', 210.
Granilla, 327.
Granite, 143.
Granulation of gunpowder, 402.
Grape, Brandy, 209; juice, Analysis of, 205; juice, Fermentation of, 206.
Grapes, Changes in, during ripening, 206; Malic acid in, 206; Tartaric acid in, 206; Treatment of, for red wine, 206; Treatment of, for white wine, 206.
Grape sugar, 181.
Graphite for glazing gunpowder, 402.
Grasses as textile fibres, 262.
"Graves," 237.
Green pigments, 358.
Green vitriol, 423.
Greens containing copper, 359.
Greenwood electrolytic process, 52.
Grey acetate of lime, 93, 95.
Grey sour, 266.
Grist, 196.
Ground nut oil, 231.
"Ground" paint, 366.
"Ground" white lead, 352.
Guaiacol, 93.
Guano, Nitrogenous, 115; Phosphatic, 115.
Guignet's green, 359.
Gum benzoin, 242; British, 186.
Gum resins, 240, 242.
Gums, 245.
Gumming of rape oil, 232.
Gun-cotton, 403; Detonation of, 404; Equation for explosion of, 404; Gas produced by explosion of, 405; Manufacture of, 404; Reconversion of, into cellulose, 404; Solubility of, 404; Specific gravity of, 404; Thermal effect of, 405.
Gunpowder, 400; Analysis of charcoal for, 401; Apparent density of, 403; Character of explosion of, 402; Charcoal for, 401; "Cocoa," 402; Equation for explosion of, 403; Exploding temperature of, 403; Gas produced in explosion of, 403; Granulation of, 402; Graphite for glazing, 402; Meal, 402; Mining, 402; Pebble, 402; Press-cake, 402; Pressure produced in explosion of, 403; Prismatic, 402; Rapidity of explosion of, 403; smoke, 403; Smokeless, 403; Sulphur for, 401; Thermal effect of, 403.
Guttapercha, 245.
Guttmann's nitric acid condenser, 10.
Gypsum, 131; as a loading material, 344.

H

Hæmatein, 324; Iso-, 325.
Hæmatite, 363.
Hæmatoxylin, 324.
Hæmatoxylon campechianum, 324.
Hair, Structure of, 257.

Half bleach, 267.
Halogens, 430.
Handlers, 388.
Handling hides, 382, 388.
Hank-dyeing, 329.
Harcourt's standard lamp, 68.
Hard pitch, 82.
Hard water, Objections to, in tanneries, 373.
Hargreaves process, 23.
Heating effect of gas burnt in different burners, 70.
Heavy spar, 430.
"Heckling" flax, 261.
Helianthin, 274.
Hellhoffite, 408.
Hemlock bark, 378.
Hemp, 261; bleaching, 267.
Hemp fibre, 261; Analysis of, 261; Tensile strength of, 261.
Henderson retort for shale distillation, 97, 98.
Hermite process, 267.
Heveene, 243.
Hexamethylpararosaniline, 290.
Hexane, 120.
Hexanitrodiphenylamine, 273.
Hide substance, Ultimate composition of, 371.
Hides, Absorption of tannin by, 395; Analysis of, 370; and skins, Quality of, 371; Breaking, 382; Butt of, 384; Cleansing and softening, 381; Defects in, 372; defined, 371; Dry-salted, 372; Green-salted, 372; Handling, 382; Liming, 382; Market, 381; Offal of, 384; Pack of, 383; Plumped, 383; "Plumping" of, 370, 372; Rounding, 384; Scudding, 384; Shaved, 389; Soaking, 381; Sweating, 384; Trimming, 384; Unhairing, 382; White arsenic for curing, 372.
Hippuric acid, 419.
Hock, 207.
Hoffmann's kiln, 136.
Hollands, 215.
Holly, Bird-lime from, 239.
Honey, 183; comb, 239; Factitious, 182.
Hoofs and horns as manure, 113.
Hop substitutes, 194.
Hopëine in hops, 194.
"Hop-backs," 198.
Hop flour, 194; meal, 194.
"Hopper salt," 20.
Hops, 194; Bleaching, 194; Choline in, 194; Condition in, 194; Hopëine in, 194; Manuring, 113; Morphine in, 194; Proximate constituents of, 194; "Sulphuring," 194; Tannin in, 194.
Horns and hoofs as manure, 113.
Horse fat, 228.
Hot press, Oil from, 229.
"Household" soaps, 249.
Huile tournante, 282.
Humulus lupulus, 194.
Hyaline layer, 368.
Hydrindigotin, 320, 322.
"Hydrocarbon" from oil gas, 75.
Hydrocarbons, "Cracking" of, in gas-making, 61.
Hydrochloric acid, 24; Impurities in, 25; in chimney gases, 24; Manufacturing yield of, 25.
Hydrocyanic acid, 241.
Hydro-extractor, 164.
Hydroferrocyanic acid, 356.
Hydrofluoric acid, 413; as an antiseptic, 413; Bottles for, 413; for etching glass, 160, 413; Manufacture of, 413; Use of, in sugar refining, 413.
Hydrogen peroxide, Bleaching by, 264, 265.
Hydrolysis, 189; of fats, 252; of fats and oils, 224; of fats by steam, 253; of fats by sulphuric acid, 253; of waxes, 225.
Hydroxyoleic acid, 235.
Hydroxyanthraquinone, 279.
Hydroxyazo-dyestuffs, Formation of, 274.
Hydroxystearic acid, 254.
Hydroxytolunaphthazine, 299.
Hygroscopic character of wool, 258.
Hymenæa, 242.
Hypogæate, Glyceryl, 231.
Hyposulphite vat for dyeing with indigo, 323.

I

IDRIAN process for making vermilion, 362.
Ilicyl alcohol, 239.
,, palmitate, 239.
Illipe oil, 227.
Illuminants in coal gas, 69.
Illuminating effect of gas burnt in different burners, 70.
,, oils, 231, 232, 233, 235, 237.
,, power of coal gas, 69.
,, value of acetylene, 74.
Incandescent gas burner, 70.

Indamine, 299.
Indamines, 303.
Indian red, 363.
,, yellow, 366.
Indiarubber, 243.
Indican, Hydrolysis of, 319.
Indicator for alkalinity, 275.
Indicators, 277, 293, 295, 302, 326, 327.
Indiglucin, 319.
Indigo, 319; Artificial, 321.
,, brown, 320.
,, carmine, 324.
,, Cause of fastness of, 322.
,, Composition of, 320.
,, Copperas vat for dyeing with, 322.
,, disulphonic acid, 324.
,, Dyeing with, 322.
,, Dyestuff similar to, 282.
,, extract, 323.
,, ,, Purple, 324.
,, gluten, 320.
,, Hyposulphite vat for dyeing with, 323.
,, monosulphonic acid, 324.
,, Printing with, 324.
,, Reduced, 322.
,, Reducing agents for, 320.
,, Solvents for, 320.
,, substitute, 304, 315.
,, sulphonic acids, Preparation of, 323.
,, Synthesis of, 321.
,, vat, Dyeing with, 322.
,, white, 320.
,, Woad vat for dyeing with, 322.
,, Yield of, 320.
Indigofera argentea, 319.
,, *tinctoria*, 319.
Indigotin, Properties of, 320; Synthesis of, 321.
Indirubin, 320, 321.
Indophenol, 304; Application of, 335; Commercial, 304.
Indophenols, 303.
Induline, 288.
Induline B, 314.
,, 3 B, 314.
,, 6 B, 314.
,, Benzene, 312.
Indulines, 312; Manufacture of, 314; Soluble, 315.
Ingrain colours, 277, 335; Developers for, 333; Dyeing with, 333.
Ingrain dyeing, Advantage of, 277; Methods of, 277.
Ink, Printing, 234.
Inks, Lithographic, 242; Red, 295.
Insecticide, Naphthalene as an, 372.
Inulin, 182.
Invert sugar, 183; Lævulose separated from, 182.
Invertase, 189, 201.
Iodine, 431; absorption, 225; Application of, 295; Extraction of, from caliche, 432; number, 225; Uses of, 432.
Iridium oxide pigment for glass, 160.
Iron buff, 328.
,, liquor, 95.
,, ,, Use of, in dyeing, 334.
,, mordants, 331.
,, pigments, 363.
,, Pyrolignite of, 95.
,, Red oxide of, 363.
,, tanning, 390.
,, Use of, in reducing nitrobenzene, 285.
Isatin, 320; yellow, 310.
Isatis tinctoria, 319.
Isinglass, 396; Composition of, 397; for fining beer, 204.
Iso-amyl cyanine, 317.
Iso-butyl alcohol, 217.
Iso-cholesterol, 258.
Iso-chromatic photographic plates, 317.
Iso-dulcitol, 326.
Iso-hæmatein, 325.
Iso-linoleate, Glyceryl, 233.
Iso-linolenic acid, 223.
,, series of acids, 226.
Isonandra gutta, 245.
Iso-oleic acid, 253, 254.
Iso-paraffins as lubricating oils, 102.
Isoprene, 243.
Iso-propyl alcohol, 217.
Iso-purpurin, 280, 281.
Iso-quinoline, 317.
Iso-ricinoleic acid, 223.
Iso-rosindulines, 313.
Ivory black, 365.

J

Japan black, 253.
,, wax, 227.
Jelly, Starch, 187.
Jet photometer, 68.
,, sugar, First, 405.
Johnson's powder, 405.
Juniper, 214.
Jute, 262; bleaching, 267; dyeing, 339; fibre, 262; fibre, Analysis of, 262; Staple of, 262.

K

Kainit, 114, 195, 426.
Kaolin, 143; as a loading material, 344; Fusibility related to composition of, 144; Zettlitz, 143.
"Keg lard," 237.
Kelp, 431.
Keratin, 257.
Keratins, 369.
Kermes, 328.
Kerosene, 121; Flashing point of, 121; Shale, 96; Standard white, 121; Water white, 121.
Kid, 390.
Kier, 265.
Kiers, 345.
Kieselguhr, 406; Specific heat of, 407.
Kieserite, 426; Block, 427.
Kiln, Claus, 33; Hoffmann's 136; Pipe, 179; Ring, 136.
Kilns, Cement, 135; Dietzsch, 135; for earthenware, 150; Lime, 128; Malt, 191; Stage, 135.
King's yellow, 361.
Kips, Arsenic, 372; defined, 371; East India, 372.
Knapp's theory of the colour of ultramarine, 355.
Knoppern, 374.

L

Laccainic acid, 328.
Lac-dye, 242, 328.
Lac, Grain, 242; Seed, 242; Shell, 242; Stick, 242.
Lacmoid, 302.
Lacquers, 242.
Lactate, Antimony, 418.
Lactic acid, 417; Ethylidene, 417; from whiskey stills, 211; Uses of, 418.
Lactose, 180.
Lævopinene, 240.
Lævulose, 182; separated from invert sugar, 182; Sweetening power of, 182.
Lager beer, 200; Pilsener, 205.
Lake, Colour, 330; Magenta, 365; "pitch," 124.
Lakes, Crimson, 328; Pigment, 365.
Lamp black, 364.
"Land phosphate," 107.
"Land pitch," 124.
Lanolin, 258; Emulsifying power of, 258.
Lanuginic acid, 271.
Lapis lazuli, 354.
Lard, 228, 237; Adulterations of, 237; as food, 237; "Bladder," 237; Cotton seed oil, an adulterant of, 237; Imitation, 232; "Keg," 237; Melting point of, 237; oil, 227, 237; oil group of oils, 227; Properties of, 237.
Latches, 380.
Laurate, Glyceryl, 236.
Laurel oil, 227.
Lauric acid, 227.
Lauth's violet, 304.
Leaches, 380.
Lead, Antimoniate, 361; Brown sugar of, 95; Caledonian White, 353; Chlorosulphite of, 353.
Lead chromate, 360; Basic, 361; basic, Dyeing with, 328; Dyeing with, 328.
Lead for vitriol chambers, 7.
,, fume, Composition of, 352.
,, glass, 157.
,, glass-pot, 158.
,, oxide for glass, 151.
,, oxide, Preparation of, 362.
,, pans, Concentration of vitriol in, 15.
,, plaster, 250.
,, Quality of, for vitriol pans, 15.
,, Red, 361.
,, soap, 250.
,, sulphate, 360.
,, sulphate, Manufacture of, from galena, 352.
,, thiosulphate, 412.
,, White, 349.
Leather, 367; Adulterations of, 392; Analysis of sole, 392; Artificial grain on, 393; Chamois, 391; Character of good, 392; Colour of, 368, 386; Curried, 389; Currying, 393; Dressed, 389; Dressing, 389; Oils for, 236, 238; Drying, 392; Dyeing, 393; Enamelled, 393; Fixing tannin in, 393; for dressing, Tanning of, 389; for dyeing, 389; for soles, Tanning of, 386; Grain of, 368; Heavy, 371; Japanned, 393; Light, 371; Morocco, 389; Patent, 393; Russia, 393; Scouring, 393; Shammy, 391; Striking the colour of, 387; Stuffed, 393; Wash, 391; White, 390; Whitening, 393; Yield of, 392.
Leathers, Content of tannin in, 395.
Leblanc process, 19.
,, soda ash, Apparent density of, 47.

Lecanora tartarea, 326, 327.
Lees, Spent, 211.
Lemon, Oil of, 241; Salts of, 417; yellow, 361.
Lepidines, 317.
"Letting down" a pigment, 360.
Leucindigo, 322.
Leuco-compounds explained, 322.
Leucomethylene blue, 306.
Levigated chalk, 354.
Levigation, 356.
Ley-boil, 266.
Lichen colouring matters, 326.
Lignin, 262.
Ligno-cellulose, 262.
Ligroïn, 120.
Lima-wood, 325.
Lime, 129; Air-slaked, 130; Bird-, 239; Bird-, from holly, 239; Blue lias, 132; -boil, 266; -bowk, 266; Brown acetate of, 93, 95; burning, Principles of, 127; Dead burnt, 130; "Fat," 127, 130; "Flare," 128; for glass, 151; Grey acetate of, 93, 95; Hydraulic, 132; -kiln gases, Carbon dioxide in, 46; kilns, Typical, 128; Over-burnt, 130; pits, 383; "Poor," 127, 130; Purification of beet juice by, 67; purifier, Action of, on coal gas, 65; Saponification by, 252; Slaked, 130; Slaking of, 130; Solubility of, 130; sour, 266; Sources of phosphate of, 107; specks, 382; Sugar recovered from molasses by, 174; used in coal distillation, 61.
Limestone, 126; Analysis of, 126.
Limestone, Analysis of blue lias, 132; of hydraulic, 126; of lime from blue lias, 133; of magnesian, 126; of Theil, 132.
Limestone, Blue lias, 132; Chemistry of burning hydraulic, 133; Dolomitic, 126; for alkali manufacture, 21; Theil, 132.
Liming hides, 382.
Limonene, 241.
Linen-bleaching, 267.
Linoleate, Glyceryl, 233.
Linoleic acid, 223.
,, series of acids, 226.
Linolenic acid, 223.
,, series of acids, 226.
Linoleum, Oils used for, 234.
Linoxyn, 233.
Linum usitatissimum, 260.
Linseed oil, 226, 233; Adulteration of boiled, 234; Baltic, 234; cake as fodder, 233; Calcutta, 234; Chemistry of drying of, 233; East Indian, 234; Grades of, 234; group of oils, 226; Oxidation of, 234; Preparation of boiled, 234; Properties of, 233; Properties of boiled, 234; Polymerisation of, in boiling, 234; Raw, 233; Refining of, 233.
Lintner's standard of diastatic power, 193.
Liqueurs, 218.
Litharge as a drier, 234.
Lithographic inks, 242.
Litmus, 327.
Lixiviation of black ash, 27.
Loading materials for paper, 344; for rubber, 244.
Loaf sugar, 180.
London deep-well water, 195.
,, gas, Statutory limit for ammonia in, 75.
Logwood, 324, 334; "Ageing" of, 324; Colours yielded by, with different mordants, 325.
"Low wines," 211.
Lubricants, Mineral, rendered viscous, 234; Rosin grease for, 242.
Lubricating oils, 231, 232, 233, 235, 236, 237, 239; from Russian petroleum, 123; Iso-paraffins in, 102.
Lubrication, Olive oil for, 231.
Lucifer matches, 411.
Lunge's bleaching process, 267.
Lupulic acid, 194.
Lupulin, 194.
Lupulus humulus, 194.
Luteolin, 326.
Lye, Spent, from soap works, 249.
Lysol, 79.

M

Machinery oil, 123.
Mactear process for alkali waste, 34.
Mactear's salt-cake furnace, 23.
"Madder," 280; bleach, 265.
Madeira, 208.
Magdala red, 301; Manufacture of, 301.
Magenta, 287, 334; Acid, 288, 336; base, 288; Dyeing properties of, 288; lake, 365; Preparation of, 287; Yield of, 288.
Magnesia, Silicate of, 263.
Magnesian limestone, Analysis of, 126.
Magnesium bisulphite for making wood pulp, 347.

Magnesium chloride, Electrolysis of, 267.
,, hypochlorite, 267.
,, manganite, 39.
,, silicate as a loading material, 344.
Magnetic separator, 196.
Main, Foul, 62; Hydraulic, 62.
Maize, germ cake as fodder, 233.
,, ,, of, removed, 186.
Maize oil, 226, 233; Properties of, 223; Yield of, 233.
Maize, Spirit from, 216; starch, 186; Starch extracted from, 186.
Malachite green, 360, 391.
Malic acid in grapes, 206.
Malt, 190; adjuncts, 193; Analysis of, 192; Diastatic power of, 192; Drying, for whiskey, 210; Green, 191; Grinding, 196; High-dried, 191; kilns, 191; Mashing, for whiskey, 210; Medium, 191; Reason of mealiness of, 193; Slack, 191; Screening, 191; screen, "Water-fall," 191; vinegar, 221; Vinegar from, 220; vinegar, White, 222.
Malted barley, "Mealiness" of, 191.
Malting, 190; Barley for, 192; Character of barley for, 190; Chemistry of, 192; difficult in summer, 191; Pneumatic, 191; Saladin system of, 191.
Malto dextrin, 196.
Maltose, 181, 197.
Manganates, 422; decomposed by water, 422.
Manganese, "Available oxygen" in, 35; borate as a drier, 234; brown, Dyeing with, 328; dioxide for purifying spirit, 216; dioxide in soap, 249.
"Manganese," Valuation of, 35; Weldon recovery process for, 37.
Manganite, Calcium, 37; Magnesium, 39; Manganous, 37.
Manganous borate, 234.
,, manganite, 37.
Manioc, 187.
Manure, Ammonium sulphate as, 112; Beet sugar sludge as a, 169; Bones for, 111; Definition of, 106; Dried blood as, 113; Drier for, 109; Farmyard, 114; General definition of, 106, 114; Horns and hoofs as, 113; Rape cake as, 116, 232; salts, 76; Sewage as, 115; Shoddy as, 113; Sodium nitrate as, 112; Soot as, 112; Water from starch factory as, 185; Wood ashes as, 114.
Manures, "Grass," 108; Nitrogenous, 112; Organic nitrogenous, 113; Phosphatic, 106; Potash, 114; Rate of assimilation of phosphatic, 111; Special, 106.
Maple sugar, 177.
Maranta arundinacea, 187.
Marble, 126.
Marc, 206; Fusel oil from brandy, 217; Olive, 231.
Margarine, 238; Coco-nut oil for, 238; Manufacture of, 238; Properties of, 238; Yellow colour imparted to, 238.
Marine animal oil, 338.
,, ,, oils, 228.
,, ,, ,, Winning of, 229.
Market bleach, 265.
Marls, Clay, 144.
Martius yellow, 273.
Masher, Steel's, 196.
Mashing, 196; and boiling, Influence of water on, in brewing, 199; Chemistry of, 196; Influence of temperature on, 197; malt for whiskey, 210.
Mash tun, 196.
Massecuite, 172, 179.
Massicot, 362.
Mastic asphalt, 125.
Matches, 408, 411; Common, 411; Composition for, 411; Extinction of glow of, 412; Head composition for safety, 411; Lucifer, 411; Rubber composition for safety, 411; Safety, 411; Waterproofed, 412; without phosphorus, 412.
Mather and Platt process, 266.
Maturing of whiskey, 212.
Mauve, 301.
Mauveine, 301.
"Mechanicals," 244.
Meilers, Charcoal burning in, 88.
Melanin, 366.
Meldola's blue, 307, 334.
Melinite, 408.
Melissic acid, 239.
Menhaden oil, 228.
Mercuric fulminate, 403.
,, iodide, 363.
,, sulphide, 362.
Mercurous chromate, 329.
"Metal," 155.
Metalepsis, 295.
Metaphenylenediamine, Formula for, 274.
Metaphosphoric acid, 409, 416.

Metatoluylenediamine, 299.
Methyl alcohol, 94; Boiling point of, 94; Specific gravity of, 94.
Methyl chloride, 429.
,, orange, 274.
,, pyridine, 105.
,, quinonediimide methochloride, 306.
,, salicylate, 241, 419.
,, violet, 289, 334.
Methylated spirit, 218.
Methylation of aniline dyestuffs, 289.
Methylene blue, 305.
,, violet, 307.
Methylpararosanilines, 289.
Mica, 143.
Milk, Cream separated from, 237.
Milk sugar, 180, 181 (see *Sugar, Milk*).
Mill-cake gunpowder, 402.
Milner's process for making white lead, 351.
Mimosa, 378.
Minium, 361.
Minor chemical manufactures, 413.
Mochyl alcohol, 239.
,, palmitate, 239.
Moëllon, 391.
Molasses, 164; Analysis of, 164; Beet, 172 (see also *Beet molasses*); Fermentation of, 215; Scheibler's process for recovery of sugar from, 175; Spirit from, 216.
Molasses, Sugar recovered from, by direct removal of potash, 176; by elution, 174; by lime, 174; by osmosis, 173; by Staffen's process, 174; by strontia, 175.
Monazo-compounds defined, 275.
Mond's chlorine recovery process, 50.
Monocalcium saccharate, 174.
"Monohydrate" sulphuric acid, 16.
Monosaccharate, Calcium, 167.
Monostrontium saccharate, 175.
Mordant, Aluminium sulphocyanide as a, 341; azo-dyestuffs, Application of, 337; Chromium acetate as a, 341; Chromium fluoride as a, 338; colours, Dyeing silk with, 339; colours, Dyeing wool with, 337; defined, 270; dyes, 330; dyes, Examples of, 334; dyestuffs, Azo-colours converted into, 337; Oxidising, 331; Non-oxidising, 331.
Mordanting by chlorination, 264.
Mordants, Acid, 331; Aluminium, 330; Basic, 330; Chromium, 331; General consideration of, 330; Iron, 331; Saddening, 330; Tin, 331.
Morin, 325.
Morocco leather, 389.
Morphine in hops, 194.
Mortar, 130; Effect of temperature on setting of, 131; "Hardening" of, 130; Setting of, 130.
Morus tinctoria, 325.
Moselle, 207.
Mother of vinegar, 219.
Moulds, 189; in yeast, 202.
Mucedin, 192.
"Multiple effect," evaporators, 170, 346.
Muriate of potash, 400.
Muriatic acid, 25.
Must, 206; Fermentation of, 206.
Mustard oil, 226.
Mycoderma aceti, 219.
Myricyl alcohol, 225.
,, cerotate, 228.
,, palmitate, 225, 239.
Myristate, Glyceryl, 238.
Myrobalans, 377.
Myrtle wax, 227.

N

Nankin yellow, 328.
Naphtha, Crude, from coal tar, 78; from petroleum, 120; "Green," 100; Mineral, for denaturing alcohol, 218; Solvent, from shale, 101; Wood, 93; Wood, for denaturing alcohol, 218.
Naphthalene, 81; as an insecticide, 372; blue, 307; Boiling point of, 81; Distillation of, 81; Enriching gas by, 73; from Russian petroleum, 123; Melting point of, 81; red, 301; Specific gravity of, 81; sulphonic acid, 385; tetrachloride, 293; Uses of, 81; Yield of, from tar, 81.
Naphthazine, 279.
Naphthenes in Russian petroleum, 123.
Naphthindophenol, 304.
Naphthindulines, 313, 315.
Naphthol blue, 304; green, 302; yellow, 273, 336.
Naphthols, Dyestuffs from, 275.
Naphthoquinone, Formula for, 279.
Naphthoquinoneoxime, 283.
Naphthoquinoneoximes, 302.
Naphthylamine, α-, 298.

Naphthyl blue, 315.
Naples yellow, 361.
Natural gas, Analysis of, 118.
Neatsfoot oil, 227, 236; Properties of, 236; Refining of, 236.
Newlands, see *Duncan*.
Night blue, 290.
Nightlights, Coco-nut oil, 251; "Stearin," 251.
Nigraniline, 312.
Nigrosines, 315.
"Ninety per cent." benzol, 79.
Nitrate of iron, Use of, in dyeing, 331.
,, Potassium, from the osmose process, 174.
,, Sodium, as manure, 112; in Glover tower, 14; commercial, Analysis of, 113; crude, Analysis of, 112; crude, Purification of, 112.
Nitrated cellulose varnishes, 246.
Nitration of benzene, 284.
,, Process of, 273.
Nitre, 400; -cake, 6; Causes of loss of, in vitriol making, 13; pot, 6; Purification of, 400; Quantity of, used in vitriol making, 13.
Nitric acid, Commercial grades of, 11; Condensation of, 9; condenser, Guttmann's, 10; Impurities in, 11; in vitriol making, 14; manufacture, 8; still, 8.
Nitrification, Process of, 113.
Nitrifying organism, 113.
Nitrite, Potassium and cobalt, 361.
Nitro-alizarin, 282.
Nitrobenzene as an oxidant, 288.
,, Manufacture of, 284; Properties of, 284; Uses of, 284.
Nitro-colouring matters, Application of, 336.
,, -compounds (dyestuffs), 273.
,, explosives, 403.
Nitrogen, Assimilation of, from air, 114; Distribution of, in coal distillation, 61; in bones, 111; in coal for alkali manufacture, 22; in shale products, Distribution of, 103.
Nitrogenous guano, 115.
,, manures, 112.
,, organic manures, 113.
Nitro-glycerin, 405; Absorbents for, 406; Equation for explosion of, 406; explosives, 405; Gas evolved by explosion of, 406; Manufacture of, 405; Properties of, 406; reconverted into glycerin, 406; Thermal effect of explosion of, 406; Yield of, 405.
Nitromonas, 113.
Nitronaphthalene for deblooming oils, 81.
Nitrophenyllactomethyl ketone, 321.
Nitroso-dimethylaniline as an oxidant, 307.
Nitrosyl sulphuric acid, 11.
Nitro-tartaric acid, 310.
"Nitrous acid," 9; Use of, in making dyestuffs, 274.
Nitrous vitriol, 13.
Non-drying oils, 224, 226.
Non-illuminant combustible gases in coal gas, 69.
Non-tannins, 378; in tanstuffs, Character of, 379.
Nordhausen sulphuric acid, 17.
Nut oils, 231.

O

Oak bark, 376.
,, galls, 374.
,, reds, 376.
Ochre, Analysis of Oxford, 364.
Ochres, 363.
Œnanthic ether, 208.
Oidium, 206.
Oil, Blue, 101; Cold drawn, 229; Constituents of crude seed, 229; Crude, from shale, 100; Crude, from shale redistillation, 100; Cylinder, 123; extractor, 230; for oil-water gas, 72; from cold press, 229; from feet of cattle, 236; from hot press, 229; gas, 74 (see *Gas, Oil*); "Green," 101; Light, from coal tar, 78; Machinery, 123; Mineral, 117; from petroleum, 121; Red, 252; resins for varnishes, 243; Rock, 117; soluble in alcohol, 235; Spindle, 123; used for linoleum, 234; Virgin, 231.
Oil, refining, Animal charcoal used in, 229; Oxidants used in, 229; Permanganate used in, 229; Sulphonic acids formed in, 229; Sulphuric acid used for, 229.
Oil-water gas, Composition of, 72.
,, Solar oil for, 72.
Oils and fats, Classification of, 226; Hydrolysis of, 224; Preparation of, 226; Properties of, 226; Properties and uses of, 231; used in soap making, 247.

Oils, Blown, 234 ; Buttery, 236 ; containing other than glyceryl salts, 228 ; containing saturated fatty acids, 227 ; containing unsaturated fatty acids, 226 ; Deblooming mineral, 122 ; defined, 233 ; Drying, 233 ; Drying, defined, 224 ; equivalents, Mean of, ascertained, 225 ; Essential, 240 ; Extraction of, by volatile solvents, 229 ; for leather dressing, 236, 238 ; for food, 231, 232, 233 ; Groups of, 226 ; Identification of, 225 ; Illuminating, 231, 232, 233, 235, 237 ; Lubricating, 231, 232, 233, 235, 236, 237, 239 ; Lubricating, from Russian petroleum, 123 ; lubricating, Iso-paraffins as, 102 ; Marine animal, 228 ; Non-drying, 224, 226 ; of cotton seed oil group, 226 ; of high viscosity, 227 ; of linseed oil group, 226 ; of olive oil group, 226 ; of rape oil group, 226 ; of the castor oil group, 227 ; of the coconut oil group, 226 ; of the cruciferæ, 226 ; of the lard oil group, 227 ; of the palm oil group, 227 ; of the sperm oil group, 228 ; of the tallow group, 227 ; of the whale oil group, 228 ; Oxidation of drying, 224 ; resins and varnishes, 223 *et seq.* ; Semi-drying, 232, 233 ; Solid, 227 ; Tanning with, 391 ; used as tanstuffs, 381 ; used in currying, 393 ; Viscosity imparted to, 234 ; which become rancid, 226, 236 ; Winning and refining of animal, 229 ; Winning and refining of vegetable, 228 ; Winning of essential, 241 ; Winning of marine animal, 229 ; won from fruit, 228 ; won from fruit seed, 228.
Okonite, 124.
Olea Europæa, 231.
Oleate, Dodecatyl, 239 ; Glyceryl, 225, 226, 227, 228, 231, 233, 236, 237 ; Sodium, 225.
Oleic acid, 223, 228 ; converted into palmitic acid, 254 ; Distilled, 253 ; Solid fatty acids made from, 255.
Oleic series, Acids of the, 226, 228.
Olein, 224, 252.
Oleo-resins, 240, 242.
Olive kernel oil, 231.
,, marc, 231.
Olive oil, 231 ; Adulterants of, 231 ; Composition of, 231 ; for lubrication, 231 ; group, Oils of, 226 ; Iodine absorption of, 231 ; Properties of, 231 ; Saponification equivalent of, 231 ; Specific gravity of, 231 ; Uses of, 231 ; Winning of, 231 ; Yield of, 231.
Olive press-cake, 231.
Olives, 231.
Omentum of pig, Fat from, 237.
O.P., 218.
Open test, Flashing point, 121.
"Open woods" (dyewoods), 325.
Orange red, 362.
Orcein, 327.
Orcellic acid, 326.
Orcellinic acid, 327.
Orchella weed, 326.
Orchil weed, 326.
Orcin, 326.
Orcinol, 326, 327.
Organised ferments, 189 ; classified, 189 ; Typical effects of, 189.
Organism, Denitrifying, 113 ; Nitrifying, 113.
Orientation of anthracene, 279.
Orleans process for making vinegar, 219.
Orpiment, 361.
Orris root, 214.
Orr's zinc white, 353.
Orthamidoazotoluene, 298.
Orthochromatic photographic plates, 295.
Orthoclase, 143.
Orthonitrobenzoic aldehyde, Formula for, 318.
Orthophenylenediamine, 298.
Orthotoluylenediamine, 298.
Oryza sativa, 185.
Osazones, 310.
Osmose process, 173 ; Apparatus for, 173 ; Potassium nitrate from the, 174.
Osmosis, Sugar recovered from molasses by, 173.
Osseine, Analysis of, 105.
Over-burnt lime, 130.
,, -proof, 218.
Oxalate, Potassium antimony, 417 ; use in dyeing, 332.
Oxalates, Acid, of potassium, 417.
Oxalic acid, 416 ; as a solvent for Prussian blue, 357 ; Impurities in, 417 ; Manufacture of, 417 ; Properties of, 417 ; Use of, in dyeing, 331 ; Uses of, 417 ; Yield of, from wood, 417.
Oxazine dyestuffs, 307.
Oxford ochre, Analysis of, 364.
Oxidant, Arsenic acid as an, 287 ; Ferric chloride as an, 305 ; Ferri-

cyanides as an, 342; Nitrobenzene as an, 288; Nitroso-dimethylaniline as an, 307.
Oxidants used in oil refining, 229.
Oxidation, Bleaching by, 264; Fusel oil removed from spirit by, 216; of alcohol, 219; of linseed oil, 234; Spongy platinum inducing, 219.
Oxide, Ferric, purifier for coal gas, 64; Spent, 265; Sulphur in spent, 65; "vessel," 65.
Oxycellulose, 272.
Oxychloride of copper, 358.
"Oxygen, Available," in manganese, 35.
Oxygen carrier, 289.
,, carriers, 288, 311.
,, for making blown oils, 235.
,, Use of, in glass making, 155.
Ozokerite, 123; candles, 252; Melting point of, 124; Refining, 129; Specific gravity of, 124.
Ozone for purifying spirit, 216.

P

Pack of hides, 383.
Paint defined, 348.
,, "Ground," 366.
,, "Mixed," 366.
Paints, 366; and pigments, 348; Vehicles for, 366.
Palmitate, Cetyl, 228, 239; Glyceryl, 228, 231, 236; Ilicyl, 239; Mochyl, 239; Myricyl, 225, 239.
Palmitic acid, 223, 227; Manufacture of, 252; Oleic acid converted into, 254.
Palmitin, 224.
Palm kernel oil, 236.
,, nut oil, 227.
,, oil, 227, 236.
,, oil group, Oils of the, 227.
,, oil, Properties of, 236.
,, pith, 187,
,, sugar, 177.
Pan process of saponification, 252.
Panclastite, 408.
Pandermite, 414.
Paper and pasteboard, 344.
Paper, Cellulose for making, 344; Loading materials for, 344; Manufacture of, from rags, 344.
Para-amidophenylamido-acridine, 318.
Para-amidophenylmethylquinoline, 316.
Para rubber, 243.
"Parachutes," 203.
Paraffin candles, 251.
,, oil, 101.
,, oil from petroleum, 121.
,, scale, 102.
Paraffin wax, 102; Decolorising, 433; from petroleum, 121; in Russian petroleum, 123; Melting point of, 102.
Paraleucaniline, Formula for, 283.
Paranitraniline, Scarlet from, 335.
Paraphenylene diamine, 299.
Pararosaniline base, Preparation of, 286.
,, Formula for, 283.
,, methylated, 289.
Paratoluidine, Condensation with sulphur, 277.
Parchment, 391.
Parian porcelain, 149.
Paris red, 362.
Parnell and Simpson process for alkali waste, 33.
Pars papillaris, 368.
,, *reticularis*, 368.
Pasteboard and paper, 344.
Paste, Manufacture of porcelain, 146; Starch, 187.
Patent blues, 336.
Pathological tannins, 375.
Peach wood, 325.
Pea-nut oil, 231.
Pearl hardening as a loading material, 344.
Peat, Destructive distillation of, 87.
Pebble gunpowder, 402.
Pectic acid, 261.
Pectin, 261.
Pectose, 261.
Pentahydroxyanthraquinone, 282.
Pentakaidecatyl alcohol, 228.
Pentane, 120.
Pentoses, 192.
Peonine, 292.
Perchlorate in Chili saltpetre, 432.
,, Potassium, in saltpetre, 401.
Perfumes, 241.
Permanganate, Potassium, 423; Bleaching by, 267; Sodium, 422; used in oil refining, 229.
Permanganates, 422.
Peroxide of hydrogen, Bleaching by, 264, 265; sodium, Bleaching by, 264.
Perry, 209; vinegar, 221.
Perseo, 327.
Persian berries, 326.

Peru balsam, 242.
Petroleum, 117; Anthracene from Russian, 123; benzine from, 120; benzole from Russian, 123; "Cracking," 119; distillation, Coke from, 122; Distribution of, 117; ether, 120; Lubricating oils from Russian, 123; Naphtha from, 120; Naphthalene from Russian, 123; Naphthenes in, 123; Origin of, 117; Paraffin oil from, 121; Paraffin wax from, 121; Paraffin wax in Russian, 123; Pitch from Russian, 123; "reduced oil," 120; Refining burning oil from, 121; Refining of, 119; Russian and American, compared, 119, 123; Solidification of, 123; Transmission of, 119; Vaseline from Russian, 123; Winning of, 118; Yellow wax from, 122.
Phenanthraquinone, 311; red, 311.
Phenazine, 297, 298.
Phenol, 80; blue, 304; Boiling point of, 80; Discoloration of, 80; Melting point of, 80; Salicylic acid prepared from, 419.
Phenolazobenzene sulphonic acid, Formula for, 275.
Phenoldisazobenzene, Formula for, 275.
Phenolphthalein, 293.
Phenosafranine, 300.
Phenylene blue, 303.
Phenylglycocine, Formula for, 321.
Phenylhydrazine, 310.
Phenylrosinduline, 315.
Phlobaphenes, 376.
Phœnix sylvestris, 177.
Phosphate, Chromium, 359; "Dicalcium," 109; "Land," 107; of lime, Sources of, 107; of soda, Application of, in calico-printing, 341; of soda, Application of, in dyeing, 338; of soda, Rhombic, 416; precipitated, 109; precipitated, Use of alkali waste in manufacture of, 109; Redonda, 107; Reverted, 109; River, 107; Soluble, 107, 108, 109.
Phosphates, Analysis of native, 108.
Phosphatic guano, 115.
,, gypsum, Analysis of, 409.
,, manures, 106.
,, ,, Rate of assimilation of, 111.
Phosphine, 287, 319.
Phosphoric acid, 416; Glacial, 416; Manufacture of, 409.
Phosphorite, 107.
Phosphorus, Distillation of, 409; Electric furnace for, 410; Manufacture of, 409; Manufacture of red, 410; Matches without, 412; Properties of red, 408; Properties of yellow, 408; Readman and Parker's process for making, 410; Refining, 410; Yield of, 410.
Photographic developer, 375.
,, plates, Orthochromatic, 295.
Photometer, Evans, 67; Jet, 68.
Photometry, 68.
Phthalein dyestuffs, 292.
Phthalic anhydride, Preparation of, 293.
Phthalophenone, 293.
Phylloxera, 206.
Physeter macrocephalus, 239.
Physetoleate, Glyceryl, 238; dodecatyl, 239.
Physical theory of dyeing, 271.
Physiological tannins, 375.
Phytosterol, 228.
Picoline, 105.
Picric acid as an explosive, 408.
,, Melting point of, 273.
,, Preparation and properties of, 273.
Pigment lakes, 365.
,, Iridium oxide for glass, 160.
,, "Letting down" a, 360.
,, Platinum, for glass, 160.
,, stannic chromate, for glass, 160.
,, style of calico-printing, 341.
,, Uranium oxide, for glass, 160.
,, Yellow, 360.
Pigments and paints, 348.
,, Black, 364.
,, Blue, 354.
,, Body of, 348.
,, Colour of mixed, 348.
,, Covering power of, 348.
,, defined, 348.
,, Dyestuffs distinguished from, 270.
,, Green, 358.
,, Iron, 363.
,, Mineral, 349.
,, Red, 361.
,, Theory of colour of, 348.
,, White, 349.
,, ,, containing lead, 352.
Pilsener lager beer, 205.
Pintsch system for oil gas, 74.

Pitch, Coal tar, 82; Composition of, 82; epuré, Composition of, 125; from Russian petroleum, 123; "Hard," 82; "Lake," 124; "Land," 124; "Soft," 82; Softening point of, 82; Stearin, 253.
"Pitching" wort, 199.
Pith, Palm, 187.
Plaster, Lead, 250.
Plaster of Paris, 131; Effect of, on fermentation of wine, 208; Setting of, 131.
Plastered wines, 208.
Plasticity related to composition of clays, 144.
Plate column, 7.
Platinum, Corrosion of, by vitriol, 15. pigment for glass, 160; Spongy, inducing oxidation, 219; stills, Concentration of vitriol in, 15.
"Ploughing" barley during malting, 191.
Plumped hides, 383.
Plumping hides, 370, 372.
Plumule, 191.
Pneumatic malting, 191.
Poisoning by white lead, Prevention of, 352.
"Poisoning the pan," 20.
Polarimeter, 198.
Polyhalite, 426.
Polyprene, 243.
Polymerisation in boiling linseed oil, 234.
Polyriciuoleic acid, 235.
Poppy-seed oil, 226.
Porcelain, 146; Berlin, 147; Biscuit, 149; clay, 144; Colouring, 148; English soft, 148; frit, 148; Glazed, 147; Glazes for, 147; Hard, 146; Parian, 149; paste, Manufacture of, 146; Reaumur's, 157; Sèvres, 148; Soft, 148.
Port, 208.
Portland cement, 134; Analysis of clay for, 138; Analysis of materials for, 138; Hardening of, 139; Materials for semi-dry process of, 134; Materials for wet process of mixing, 134; Setting of, 139.
Pot-ale, 211.
Pot, Nitre, 6; still, 211.
Potash, Caustic, 428; from beet sugar residues, 428; from suint, 429; from wood ashes, 428; from yolk, 429; glass, 157; Manufacture of carbonate of, 428; manures, 114; Red prussiate, 434; salts, 426; soap, 247; Sugar recovered from molasses by direct removal of, 176; Yellow prussiate of, 433.
Potashes, 427.
Potassium aluminium sulphate, 424.
,, antimony oxalate, Use of, in dyeing, 332.
,, bichromate, 421.
,, bromide, 431.
,, carbonate, 427.
,, chlorate, Manufacture of, 42.
,, ,, Separation of, by cooling, 42.
,, chloride, Winning of, 426.
,, chromium sulphate, 426.
,, cyanide, 434.
,, ferrocyanide, 433, 434.
,, ,, Uses of, 434.
,, iodide, 432.
,, nitrate, 400.
,, ,, from the osmose process, 174.
,, perchlorate in saltpetre, 401.
,, permanganate, 433.
,, ,, bleaching by, 267.
,, ,, for purifying spirit, 216.
,, salts, Sources of, 427.
,, sulphate, 427.
,, sulphocyanide, 434.
,, thiocyanate, 434.
,, ultramarine, 355.
Potato, Saccharification of starch in, 215; spirit, 215, 216; starch, 184.
Potatoes, Diseased, used for starch making, 185; for starch, 184; Frost-bitten, 184; Fusel oil from, 217; Loss of starch in, by frost, 184; Loss of starch in, by oxidation, 184; Specific gravity of, indicating starch content, 184.
Pottery clays, Analysis of, 143; Properties of, 143.
Pottery, Kinds of, 146.
Poudrette, 115.
Precious stones, Imitation, 158.
Precipitation processes of making white lead, 351.
Preservative, Salicylic acid as a, 416; Saltpetre as a, 401.
Press-cake, Gunpowder, 402; Olive, 231.
Press, Filter, 168; Hydraulic, 229.
"Pressure bowl," 340.
Priming beer, 204.
Primuline base, 277.
,, dyestuffs, 277.

Primuline, Method of dyeing with, 278.
,, Photographic application of, 278.
,, yellow, 277.
Printing, albumin, Application of, in calico, 341; Application of acetic acid in cotton, 340; Arsenate of soda, Application of, in calico, 341; Block, 340; blood albumin, Application of, in calico, 341; Calico, 340; Colour, 340; Discharge style of calico, 341; Dyeing style of calico, 341; ink, 234; phosphate of soda, Application of, in calico, 341; Pigment style of calico, 341; Resist style of calico, 342; Roller, 340; Steam style of calico, 340; Styles of cotton, 340; Thickening agents for calico, 340; with aniline black, 311; with indigo, 324; Wool, 342.
Producer gas, 72; Composition of, 60; for retort furnace, 59.
Proof spirit, 218; Specific gravity of, 218.
"Proof stick," 179.
"Proof vinegar," 221.
Propyl alcohol, 217.
Protocatechuic acid, 376.
Prune, 308.
Prussian blue, 356; Dyeing with, 328; Manufacture of, 356; Oxalic acid as a solvent for, 357; Solubility of, 357; Soluble, 357.
Prussiate of potash, Red, 434; Yellow, 433.
Pseudo-indoxyl, 321.
Puer, 384.
Pugmill, 366
Purifier, Arrangement of gas, 65; for coal gas, Ferric oxide, 64; Lime, Action of, on coal gas, 65; Revivification of spent, 64.
Purifiers, Gas, 64.
Purpurine, 280.
Purrée, 366.
Putrefaction applied in winning oils, 229.
Puzzuolana, 140; Analysis of, 140.
Puzzuolanic cement, 140.
Pyridine, 105; bases, 78; bases for denaturing spirit, 219; Methyl, 105.
Pyrites, 2.
,, burners, 2; Dust from, 6.
,, gases, Percentage of oxygen in, 3; Percentage of sulphur dioxide in, 3.
Pyrites smalls, 2; burner, 5.
,, spent, Sulphur in, 3.
Pyritic shale, 425.
Pyrocatechol, 298. 376; tannins, 376.
Pyrogallic acid, 375.
Pyrogallol, 375; Application of, 295; tannins, 376.
Pyrogallolphthalein, 295.
Pyrolignite of iron, 95.
Pyrrol, 105; red, 105.

Q

Quandel, 88.
Quarter bleach, 267.
Quassia, a hop substitute, 194.
Quebracho, 378.
Quercitannic acid, 374.
Quercitin, 326.
Quercitrin, 326.
Quercitron bark, 326.
Quercus ægylops, 377.
,, *castanea*, 376.
,, *cerris*, 376.
,, *ilex*, 328.
,, *infectoria*, 374.
,, *robur*, 376.
,, *tinctoria*, 326.
Quick vinegar process, 220.
Quinaldine, 317.
Quinoline derivatives (dyestuffs), 316.
,, from coal tar, 317.
,, red, 317.
,, yellow, 317.
Quinonedichlorimide, 303.
Quinone derivatives (dyestuffs), 278.
Quinonedi-imide, 303.
Quinonedioxime, 302.
Quinone dyestuffs, Application of, 279.
Quinoneoximes, 282, 302.
"Quinonoid structure," 278.
Quinophthalone, 317.

R

Rack-a-rock, 408.
"Racking-back," 204.
Racking beer, 204.
Raffinose in beet juice, 165.
Rags, Manufacture of paper from, 344.
Rancid butter, Butyric acid in, 237.
Rancid, Oils which become, 226, 236.
Rancidity, Cause of, 224; Chemistry of, 224.
Rape cake as manure, 116, 232.
Rape oil, 226, 232; Blown, 234; group, Oils of, 226; Gumming of, 232; Properties, of, 232; Uses of, 232; Yield of, 232.

Rapic acid, 223.
Rasping machine, 184.
Rave's treatment of vitriol tar, 101.
Readman and Parker process of phosphorus manufacture, 410.
Realgar, 361.
Reaumur's porcelain, 157.
Rectification of crude spirit, 217.
Rectified spirit of wine, 218.
,, Specific gravity of, 218.
Rectifier, 212.
Red arsenic, 283.
,, lead, 261.
,, liquor, 29.
,, Caustic soda from, 31.
,, oxide of iron, 363.
,, phosphorus, Manufacture of, 110,
,, ,, Properties of, 408.
,, pigments, 361.
,, vegetable colouring matters, 326.
Redistillations, Crude oil from shale, 100.
Redonda phosphate, 107.
"Reduced oil," petroleum, 120.
Reduction, Bleaching by, 264.
Refined alkali, 29.
Refrigerators used in brewing, 198.
Regenerative burner, 70.
Rendering fats, 229.
,, of tallow, 236.
Reseda luteola, 326.
Resins, 241; defined, 240; for varnishes, 246; Gum, 240, 242; Oleo, 242; Running, 245; varnishes and oils, 223.
Resists, 342.
Resist style of calico-printing, 342.
Resorcin green, 302.
Resorcinol, Application of, 293; Preparation of, 294; Properties of, 294.
Resorcinolazobenzene, Formation of, 276.
Resorcinoldisazobenzene, Formation of, 276.
Resorcinolphthalein, 294.
Resorufin, 308.
Retort carbon, 61.
,, Dimensions of gas furnace, 58.
,, gas furnace, 58.
,, Henderson, for shale distillation, 97, 98.
,, Percentage of coke needed for firing gas, 58.
,, Producer for gas furnace, 59.
,, Scurf, 61.
,, Young & Beilby, for shale distillation, 97, 99.
Retorts, Carbonising in, for gas production, 58; Carbonising wood in, 90; Charging gas, 60; Drawing gas, 60; Mechanical charging of gas, 60; Process of distillation in gas, 60.
"Retted" flax, 260.
"Retting" flax, 260.
Reversion of superphosphate, 109.
Reverted phosphate, 109.
Revivification of spent purifier, 64.
Revolver black ash process, 26.
Rhamnotin, 326.
Rhamnus amygdalinus, 326.
,, *frangula*, 401.
Rhigolene, 120.
Rhodamine, 297, 334; S, 297.
Rhombic phosphate of soda, 416.
Rhus coriaria, 377.
,, *cotinus*, 325.
,, *japonica*, 374.
,, *semialata*, 374.
Rice starch, 184, 185.
Ricinine, 235.
Ricinoleate, Glyceryl, 235.
Ricinoleic acid, 223, 227.
,, series of acids, 226.
Ricinus communis, 235.
Rinmann's green, 360.
"Rippling" flax, 260.
"River phosphate," 107.
Roans, 389.
Roasters, Blind, 23; Open, 23.
Roburite, 408.
Roccella fuciformis, 326.
,, *tinctoria*, 326.
"Rock," 252.
Rocks, Influence of rate of cooling on structure of, 157.
Roller printing, 340.
Roman cement, Analysis of, 133.
Rope, 261.
Ropy fermentation of beer, 204.
Rosaniline, 287; base, 288; base, Chemistry of, 287; Constitution of, 284; hydrochloride, 288; salt, Formation of, 287; Triphenyl-, 290.
Rosin, American, 241; Common, 241.
Rosinduline, Phenyl, 315.
Rosin grease, 242.
,, oil, 242.
,, Properties of, 242.
,, spirit, 242.
,, White, 242.
Rosolic acid, 292.
Rotatory exhauster, Beale's, 62.
Rouge, 18, 363.
Rounding hides, 384.

Rove, 374.
Rubber, Adulterations of, 244; Black vulcanised, 244; Cause of perishing of, 244; Ceara, 243; Loading materials for, 244; Para, 243; Red vulcanised, 244; Solvents for, 243; Surrogates for, 244; Vulcanisation of, 244; Vulcanised, 243; vulcanised, Constitution of, 244; vulcanised, Properties of, 244.
Ruberythrin, 280.
Rubia tinctoria, 280.
Rum, 215.
Rumex hymenosepalum, 378.
"Running" resins, 245.
Rusma, 383.
Russia leather, 393.
Russian petroleum, 123 (see also *Petroleum*).
,, tar, 93.
,, turpentine, 240.

S

"Saccharate," 163; Calcium, 167; Distrontium, 175; Monocalcium, 174; Monostrontium, 175; Tricalcium, 174.
Saccharates, 174.
Saccharatum, Sorghum, 177.
Saccharides, 162.
Saccharification of starch in potato, 215.
Saccharine, Manufacture of, 420.
Saccharinum, Acer, 177.
Saccharomycetes, 189, 200.
Saccharomyces cerevisiæ, 202.
,, *ellipsoïdeus*, 206.
Saccharum officinarum, 162.
Saddening mordants, 330.
Safranine, 334; T, 300.
Safranines, 299.
Safety matches, 411 (see also *Matches*).
Safflower, 326.
Safrosin, 295.
Saggers, 147.
Sago, 187.
Saladin system of malting, 191.
Salicylate, Methyl, 241, 419.
Salicylic acid, 419; as an antiseptic for beer, 209; as a preservative, 420; natural, 419; prepared from phenol, 419.
Salt, 19; Analysis of rock, 19; Bay, 20.
Salt cake, Composition of, 24; furnace, 22; furnace, Mactear's, 23; Manufacture of, 22; Yield of, 23.
Salt, Calcium sulphate in rock, 19.
"Salt fishing," 20.
Salt from sea-water, 21.
"Salt gardens," 21.
Salt glazing, 149.
,, pans, 20.
,, Rock, 19.
Saltpetre as a preservative, 401.
,, Bengal ordinary, 400.
,, earths, 400.
,, flour, 400.
,, Perchlorate in Chili, 432.
,, Potassium perchlorate in, 401.
Salts, 420.
Samming, 392.
Sandblast, 160.
Sanitas, 240.
Santal wood, 325.
Santorin earth, 140.
Sapan wood, 325.
Saponification, 225, 247, 248; by lime, 252; equivalent, 226; of fats, 225; Pan process of, 252; processes, Yield in, 253; with alkali carbonates, 247.
Saturated fatty acids, Oils containing, 227.
Saucers of vitriol chambers, 7.
Saxony blue, 323.
"Scale, Crude," 101.
Scale, Paraffin, 102.
"Scars," 3.
Scheele's green, 359.
Scheibler's process for recovery of sugar from molasses, 175.
Schizomycetes, 189.
Schlempe, 428.
Schlempekohle, 176, 428.
Schultze's powder, 405.
Schweinfurth green, 359.
Scott's cement, 132.
Scouring cotton, 265.
,, leather, 393.
,, wool, 258.
Screening malt, 191.
"Scrim," 234.
Scudding hides, 384.
Scurf, Retort, 61.
"Scutching" flax, 261.
Sealing wax, 242.
Seal oil, 228, 239.
Sea-water, Analysis of, 21; Salt from, 21.
Seaweed, 431.
Sebaceous glands, 368.
Seed-lac, 242.

Seed, Oils won from, 228.
Seger's cones, 147.
Semi-rotation, 181.
Separator, Magnetic, 196.
Sepia, 365.
Sepia officinalis, 365.
Septaria nodules, 133.
Sericin, 259; removed from raw silk, 259.
Sesame oil, 226, 233; Properties of, 233; Uses of, 233.
Sesamum orientale, 233.
Sesquicarbonate, 30.
Sesquiterpenes. 240.
Setting of mortar, Effect of temperature on, 131.
,, Portland cement, 139.
"Settling back," 204.
Sewage as manure, 115.
,, precipitants, 424.
Sèvres porcelain, 148.
Shale, benzine from, 101; benzoline from, 101; Composition of, 96; Crude oil from, 100; Crude oil from redistillation, 100; Destructive distillation of, 96.
Shale distillation, Ammoniacal liquor from, 102; Gas from, 103; Gasolene from, 103; Henderson retort for, 97, 98; Young and Beilby retort for, 97, 99.
Shale "green oil," 101.
,, kerosene, 96.
,, Naphtha solvent from, 101.
,, oil, Purifying, 101.
,, oil, Yield of products from crude, 102.
,, Origin of, 96.
,, products, Distribution of nitrogen in, 103.
,, Pyritic, 425.
,, Yield of products from Broxburn, 97.
"Shales, Vitriol," 17.
Shammy leather, 391.
Shark liver oil, 228.
Shaved hides, 389.
Shellac, 242.
Sherry, 208; Caramel for colouring, 208; cask, Use of, for maturing whiskey, 212.
Shoddy as manure, 113.
Shot effects in dyed silk, 338.
Siemens burner, 70.
,, tank furnace, 144.
,, toughened glass, 156.
Sienna, Burnt, 364; Raw, 364.
Siennas, 363.
Silent spirit, 217.
Silica for glass, 151.
Silicate of magnesia, 263.
Silk, 259; Analysis of raw, 259; Artificial, 259; bleaching, 264; "Boiled-off," 265; Denitration of artificial, 260; "Discharging," 265.
Silk dyeing, 386; with acid colours, 339; with basic colours, 338; with direct colours, 338; with mordant colours, 339.
Silk fibre, 259; Behaviour of, to reagents, 259; Specific gravity of, 259.
Silk glue, 259.
,, Sericin removed from raw, 259.
,, "Stripping," 265.
,, "Tussur," 259.
,, "Ungumming," 265.
,, Winding, 259.
Silks, Wild, 239.
Silver ultramarine, 355.
Simon-Carvès coke oven, 86.
,, oven, Yield of products from, 87.
Simpson and Parnell process for alkali waste, 33.
Sintering, 148.
Size, 397.
"Skimming back," 203.
Skimming system of cleansing beer, 203.
Skin, Proximate composition of, 369; Structure of, 367.
Skin-hardened soaps, 249.
Skins and hides, Quality of, 371.
,, defined, 371.
,, Falling of, 373.
,, Ultimate composition of, 371.
Skivers, 389.
Slack malt, 191.
Slag, Analysis of basic, 110; Ball mill for basic, 111; Basic, 110; Cement, 141; for cement, Blast furnace, 140; wool, 263.
Slaked lime, 130.
Slaking of lime, 130.
Sleekers, 393.
Slurry, Analysis of cement, 138; Manufacture of, 134.
Small coal for alkali manufacture, 22.
Smalls burner, Pyrites, 5.
,, Pyrites, 2.
Smalt, 159, 357; Analysis of, 357.
Smoke, Gunpowder, 402.
Smokeless powder, 403.
Soaking hides, 381.
Soaks, 381.
Soap, 247; and candles, 247; Artificial mottled, 248; Cold-water,

248; Curd, 248; Detergent action of, 250; Detergent properties of, enhanced by alkaline substances, 247; "Figging" in soft, 249; Filling materials for, 247; Fitted, 248; Frothing prevented in whiskey stills by, 211; Glass-makers', 152; Green colour of soft, 249; Lead, 250; lyes, Glycerine recovered from, 249; -making, Fats and oils used in, 247; Manganese dioxide in, 249: Manufacture of, 248; Manufacture of soft, 249; Mottled, 248; Potash, 247; Primrose, 248; Sodium sulphate in, 247; Sugar in, 248; Use of, in dyeing, 332; Water in, 248; Yellowing of wool by, 264.
Soaps, defined, 247; Household, 249; Milling, 249; Raw materials for, 247; Scouring, 249; Soda, 247; Toilet, 249; Transparent, 249.
Soapstone, 344.
Soda, Analysis of crude nitrate of, 112; ash, 28; ash, Analysis of, 29; Apparent density of ammonia, 47; ash, Apparent density of Leblanc, 47; ash, Causticising, by fusion with ferric oxide, 47; Bicarbonate of, 30; Caustic, 30; Caustic, from red liquor, 31; crystals, 29; "glass," 157; Grades of caustic, 31; liquor, Concentration of caustic, 31; Purification of crude nitrate of, 112; soaps, 247; Ultramarine, 354; Washing, 26.
Sod-oil, 391.
Sodium alizarate, 281.
,, aluminate, Use of, in dyeing, 331.
,, arsenate, Manufacture of, 416.
,, ,, Use of, in dyeing, 330.
,, bicarbonate, Conversion of, into soda ash, 46.
,, bichromate, 421.
,, bisulphite, 6.
,, "carbolate," 79.
,, carbonate prepared from cryolite, 51.
,, chlorate, 43.
,, ,, for alizarin manufacture, 281.
,, chloride, Effect of, in water for brewing, 199.
,, chromate, 421.
,, citrate as a resist, 342.
Sodium ferrite, 47.
,, fluoride as an antiseptic for beer, 204; as a softening agent, 413.
,, metaborate, 415.
,, nitrate as manure, 112.
,, ,, Commercial analysis of, 113.
,, ,, in Glover tower, 14.
,, ,, Use of, in making dyestuffs, 274.
,, oleate, 225.
,, oxalate, 417.
,, permanganate, 422.
,, peroxide, Bleaching by, 264.
,, phenyl carbonate, 420.
,, phosphate, Manufacture of, 416.
,, ,, Use of, in dyeing, 330.
,, sesquicarbonate, 30.
,, sulphate for glassmaking, 24.
,, ,, in soap, 247.
,, ,, Use of, in dyeing, 335.
,, sulphide as a depilatory, 383.
,, ,, for making wood pulp, 346.
,, sulphite, 6.
Sodoxyanthraquinone, 281.
Soffioni, 414.
Softening processes in tanning, 384.
"Soft pitch," 82.
" ,, woods" (dyewoods), 325.
Solar oil, 123; for oil water gas, 72.
"Solid flame burners," 70.
,, green, 302.
Solidification of Russian petroleum, 123.
Solidified bromine, 431.
,, sulphuric acid, 16.
Soluble blues, 290.
Solution of metals in glass, 158.
Solutions, Action of, on glass, 161.
"Solvent naphtha," 79; from shale, 101.
Solvents, 434; Spirit, for varnishes, 246; Volatile, 230; Volatile, for wool washing, 258.
Soot, Ammonia in, 112; Arsenic, 415; for manure, 112.
Sorghum saccharatum, 177.
,, sugar, 177.
Sorrel, Salts of, 417.
Sour beer, 204.
Sour, Grey, 266.
,, Lime, 266.
"Sour" process of starch extraction, 186.
,, tanning, 387.

Sour, White, 266.
Soxhlet extractor, 229.
Sparger, 196.
Sparging, 196.
Speise, 357.
Spent beet, Analysis of, 167.
,, lees, 211.
,, lye from soap works, 249.
,, oxide, 2, 65.
,, ,, Sulphur in, 65.
,, purifier, Revivification of, 64.
,, pyrites, Sulphur in, 3.
,, tan, 380.
,, ,, Application of, in making white lead, 350.
,, wash, 214.
,, ,, as a fodder, 216.
Spermaceti, 239; Adulterations of, 239; Properties of, 239.
Sperm candles, 252.
,, oil, 228, 239.
,, ,, group, Oils of, 228.
,, ,, Properties of, 239.
Spindle oil, 123.
Spirit, 209; Analysis of, 216; blue, 290; Chromic acid for purifying, 216; Clean, 211; Commercial, 215; Composition of, 217; Content of fusel oil in crude, 216; Denatured, for varnishes, 219; from maize, 216; from molasses, 216; from turnips, 216; Fusel oil removed from, by oxidation, 216; German, 215; German system of denaturing, 219; Manganese dioxide for purifying, 216; Materials for manufacture of, 209; Methylated, 218; methylated, New, 218; methylated, Old, 218; of wine, Rectified, 218; oil of turpentine, for denaturing, 219; Ozone for purifying, 216; Potassium permanganate for purifying, 216; Potato, 215, 216; Proof, 218; proof, Specific gravity of, 218; Purification of crude, 216; Pyridine bases for denaturing, 219; Rectification of crude, 217; rectified, Specific gravity of, 218; Removal of fusel oil from crude, 216, 217; Silent, 217; Valuation of crude, 216; varnishes, 246; varnishes, Solvents for, 246; Wood, 93; Wood charcoal for purifying, 216; wood, Composition of, 94.
Spirits, Caramel for colouring, 182; Classification of potable, 209; of turpentine, 240.
Spray, Water in vitriol making, 11.
Sprengel's explosives, 407.
Stack process of making white lead, 349.
Staffen's process, Sugar recovered from molasses by, 174.
Stage kilns, 135.
Staining wood, 423.
Staking skins, 390.
Stannate of soda, Use of, in calico-printing, 331.
Stannic chloride, Use of, in dyeing, 231.
Stannic chromate, pigment for glass, 160.
Stannous acetate as a discharge, 341.
,, chloride as a discharge, 341.
,, ,, Use of, in dyeing, 331.
"Staple" of cotton, 260; of flax, 261; of jute, 262; of wool, 257.
Starch, 183; and sugar, 162; Arrow-root, 183, 187; Colloidal character of, 187; converted into sugar, 182; extracted from maize, 186; extracted from rice, 186; extraction, Sour process of, 186; extraction, "Sweet" process of, 186; factory, Residue from, as fodder, 185; factory, Water from, as manure, 185; gelatinisation of, 187; granules, Sizes of, 183; "Green," 184; jelly, 187; Laundry, 185; Maize, 186; making, Diseased potatoes used for, 185; manufactured from wheat, 185; manufacture, Gluten recovered in, 186; manufacture of, 184; paste, 187; Potato, 184; Potatoes for, 184; Rice, 184, 185; Saccharification of, in potato, 215; separated from gluten by caustic soda, 188; separated from gluten by fermentation, 185; solution, Viscosity of, 187; Sources of, 183; sugar, 181; sugar, Caramel made from, 182; sugar, Composition of, 182; sugar, Manufacture of, 182; Uses of, 187; Wheat, 185; Yellow tint of, corrected, 187; yielding materials, Analysis of, 183.
Starches, Edible, 187; for brewing, 193.
Stassfurt boracite, 414.
Stassfurtite, 414.
Stassfurt salt deposits, 426.
Steam style of calico-printing, 340.
Stearate, Glyceryl, 228, 237.
Stearic acid, 223; Manufacture of, 252.

Stearin, 224; Cotton seed, 232; Cotton seed, an adulterant of tallow, 237; for candles, 252.
"Stearin" nightlights, 251.
Stearin pitch, 253.
,, (stearic acid) candles, 255.
Stearo-lactone, 255.
Stearoptenes, 241.
Steatite, 344.
Steel's masher, 196.
Steeping barley, 190.
"Stench" of beer, 194.
Sterilised air for refrigerating rooms, 198.
Stick lac, 242.
Stockholm tar, 93.
Stone, Alum, 424; Analysis of, 421; Artificial, 141; Blue, 423; China, 148; Cornish, 149; square system of cleansing beer, 203.
"Stone, Vitriol," 18.
Stones, Imitation precious, 158.
Stoneware, 149; Glazes for, 149.
Stout, 205; Water for, 195.
"Stoving," 264.
Strass, 158.
Straw, Charcoal from, 402.
"Striking out" leather, 292.
,, the colour of leather, 287.
"Stripping" silk, 265.
Strontia, 429; burning, 176; process, 175; Sugar recovered from molasses by, 175.
Strontianite, 176, 429.
Strontium carbonate, 176.
,, hydroxide for sugar refining. 176.
,, ,, Preparation of, 176, 430.
,, nitrate, 429.
,, salts, 429.
Stucco, 132.
Stuffed leather, 393.
Stuffing skins, 390.
Styles of cotton printing, 240.
Styrax benzoin, 242.
"Sublimed white lead," 352.
Substantive dyes, 270; Examples of, 333.
,, dyestuffs defined, 270.
Succinic acid, 201; produced in acetic fermentation, 219.
Sucrates, 174.
Sucrose, Hydrolysis of, 183.
Sucroses, 162.
Sudoriferous glands, 368.
Suet, 238.
Sugar and starch, 162.
Sugar, Beet, 165; beet, Diffusion process of extraction, 165; Beet, identical with Cane sugar, 177; Cube, 180; candy, 180.
Sugar, Cane, 162. 163; Composition of raw, 165; Extraction of, 163; Hydrolysis of, 183; Inversion of, 183; juice, Analysis of, 163; juice, Composition of raw, 165; juice, Concentration of, 163.
Sugar, Caramel, made from starch, 182; Composition of raw, 177; Composition of refined, 180; Composition of starch, 182; Compounds of, with alkaline earths, 174; converted into starch, 182; Decolorisation of, 178; Defecation of, by blood, 178; defined, 162; Demerara, 177; diffusion process, Battery of cells for, 166; diffusion process, Cells for, 166; extraction, Composition of sludge from beet, 169; extraction, Diffusers for, 166; extraction from beet. 165; Fermentation of, 201; Fermentation of cane, 201; filtration, Twill bags for, 178; First jet, 172; for diabetic patients, 182; Fruit, 182: in soap, 248; Invert, 183; Loaf, 180; loaves, 180; Lump, 180; Manufacture of starch, 182; Maple, 177; Moist, 177; "Moist" fraudulently coloured, 179; Milk, 180; milk, Extraction of, from milk, 181; milk, Fermentation of. 201; milk, Solubility of, 181; Minor sources of, 176; of fruits, 181; of lead, Brown, 95; Palm, 177; Preparation of, for the market, 180; Recovered from molasses (see *Molasses*).
Sugar recovery, Aluminium sulphate used for, 176; Baryta used for, 176; Strontium hydroxide for, 176.
Sugar refining, Animal charcoal used in, 178; Char for, 178; Evaporation of liquor in, 179; hydrofluoric acid, Use of, in, 413; Raw, 177.
Sugar, Scheibler's process for recovery of, from molasses, 175; Solubility of milk, 181; solution, Filtration of, 178; Sorghum, 177; Starch, 181; Tin in Demerara, 180; Utilisation of uncrystallised, 172; vinegar, 221; White, 180; Yellow colour of, corrected, 180; Yield of, from beet, 172.

Sugars classified, 162.
,, for brewing, 193.
,, Nomenclature of, 162.
Suint, 258; Potash from, 429.
Sulphate ultramarine, 354.
Sulphates, 423.
Sulphazines, 304.
Sulphide vessel, 65.
Sulphite liquor, Spent, 347.
,, process for making wood pulp, 347.
Sulphites, Bleaching by, 264.
Sulphocyanide, Potassium, 434.
Sulphoglyceric acid, 405.
Sulphonation, Process of, 273.
Sulphonic acid dyestuffs, Application of, 366.
,, acids formed in oil refining, 229.
Sulphur, Black, 255; Blue, 255; burners for vitriol making, 5; burners, Percentage of oxygen in gases from, 5; burners, Percentage of sulphur dioxide in gases from, 5.
Sulphur chloride, 437; process of vulcanisation, 244.
Sulphur compounds in coal gas, 68; Determination of, 68.
Sulphur dioxide and oxygen, Combination of, 18.
Sulphur dioxide, Bleaching by, 264; Boiling point of, 6; Conversion of, into sulphuric acid, 11; from blende, 5; from sulphuretted hydrogen, 5; Liquefied, 6; manufacture, 6; Percentage of, in gases from sulphur burners, 5; Specific gravity of, 6.
Sulphur, Distillation of, 401; Flowers of, 2; for gunpowder, 401; Ignition point of, 402; in spent oxide, 65; in spent pyrites, 3; Methods of extracting, 1; Native, 1; Recovered, 1, 33; recovery from alkali waste, 32; recovery from gas liquor, 76; sprinkled on hops, 194.
Sulphuretted hydrogen in coal gas, 68.
,, ,, Sulphur dioxide from, 5.
Sulphuric acid, Action of, on castor oil, 235; Arsenic in, 16; Conversion of sulphur dioxide into, 11; English, 17; for Gay-Lussac tower, 13; Fuming, 17; Hydrolysis of fats by, 253, 254; Impurities in, 16; in vinegar, 221; manufacture (see *Vitriol*); Monohydrate, 16; Nordhausen, 17; "Solidified," 16; Specific gravity of, 17; Use of, for oil refining, 229; Uses of fuming, 18.
Sulphur dioxide, Percentage of, in pyrites gases, 3.
Sulphuric anhydride, 18.
Sulphuring hops, 194.
Sulphurous acid, Antiseptic, for beer, 204.
Sumach, 377; Use of, in dyeing, 332.
Sumachtannic acid, 374.
Sunflower oil, 226.
Superphosphate, 107; "Double," 109; Evaluation of, 109; from bone ash, 111; Reversion of, 109.
Surrogates for rubber, 244.
Suspender liquor, Composition of, 388.
Suspenders, 386.
Swarf, 285.
Sweat glands, 368.
Sweat, Wool, 258.
Sweating hides, 384.
Sweetened gin, 214.
Sweet fennel, 214.
Sweetmeats, Dextrose for, 182.
Sweet process of starch extraction, 186.
Sweet-water, 256.
Sylvestrene, 240.
Synthetic dyestuffs, Organic, 273.

T

Tallow, 236; Adulterations of, 237; Beef, 228, 236; Bone fat as adulterant of, 237; Cotton seed stearin as adulterant of, 237; dips, 251; group, Oils of the, 227; Hardening of, 237; Melting point of, 237; Mutton, 228, 236; oil, 227; Properties of, 237; Refining of, 237; Rendering of, 236.
Tan liquors, Acids in, 379.
Tan, Spent, 380; Application of, in making white lead, 350.
Tank liquor, Analysis of, 28; Carbonation of, 28; Evaporation of, 29; Purifying, for caustic soda, 30.
Tank waste, 28, 32; Treatment of, 32.
Tanneries, Water for, 372.
Tannic acid, Preparation of, 375; Properties of, 375; Use of, in dyeing, 331.

Tannin, Absorption of, by hides, 395; Alcohol, 375; Content of, in leather, 395; Crystal, 375; defined, 374; Ether, 375; Extraction of, from galls, 374; Fixing, in leather, 393; in hops, 194; Use of, in dyeing, 331; Water, 375.
Tanning, Chrome, 390; Electric, 388; "Extracts" for, 380; Finishing processes in, 392; Function of acids in, 387; Iron, 390; materials, Analysis of, 379; Preparatory processes in, 381; processes, 386; processes classified, 367; processes, Rapid, 388; Softening processes in, 384; Sour, 387; Theory of, 394; with alum, 390; with mineral salts, 389; with oils, 391.
Tannins, Bloom deposited by, 376; Classification of, 376; Nomenclature of, 374; Pathological, 375; Pyrocatechol, 376; Pyrogallol, 376; Physiological, 375.
Tanstuffs, 373; Analysis of, 379; classified, 374; Extraction of, 380; non-tannins in, Character of, 379; Mineral salts used as, 381; Oils used as, 381.
Taps, 380.
Tar acids, 79.
,, Beckton, Composition of coal, 77.
Tar, Black, 101; Coal, 76; Constituents of coal, 76; Crude naphtha from coal, 78; Distillation of coal, 77; distillation, Products from coal, 77; Enriching gas by, 74; First runnings from coal, 78; from cannel, 71; Light oil from coal, 78; Naphthalene yield from, 81; Russian, 93; Stockholm, 93; "Vitriol," 101; "vitriol," Rave's treatment of, 101; Wood, 92; Yield of, by different coals, 76; Yield of, from coal, 66; Yield of from Simon-Carvés oven, 82.
Tartar, 418.
Tartar emetic, Use of, in dyeing, 331.
Tartaric acid, 418; Impurities in, 418; in grapes, 206; Solubility of, 418; Use of, in dyeing, 330; Uses of, 418.
Tartrate, Calcium, 418.
Tartrazine, 310.
Tartrazines, 309.
Tawing, 390.
Taylor filter, 178.
Temperature measured by Seger's cones, 147.
***Terminalia chebula*, 377.**
Terpenes, 240.
***Terra japonica*, 377.**
***Terre verte*, 360.**
Tetrabromofluorescein, 294.
Tetrahydroxyanthraquinones, 282.
Tetraiodofluorescein, 295.
Tetraiodopyrrol, 105.
Tetramethyldiamidobenzophenone, 290, 309.
Tetramethylindaminesulpho-sulphonate, 306.
Tetrazo-compounds defined, 275.
Tetrazodiphenyl chloride, 277.
Tetrazo-dyestuffs, 275; Formation of, 276.
Textile fibres, 257; Grasses as, 262.
Thallium glass, 160.
Theil limestone, 132; Analysis of, 132.
Thermometer of constant zero point, 160.
Thermometers, Glass for, 160.
Thiazines, 304.
Thickening agents for calico-printing, 340.
Thiocarmine, 336.
Thiocyanate, Potassium, 434.
Thionine, 304.
Thiosulphate, Calcium, 363.
"Thirty per cent." anthracene, 82.
Tiles, 145; Encaustic, 145.
Til-seed, 233.
Tincal, 414.
Tin crystals, Use of, in dyeing, 331.
,, in Demerara sugar, 180.
,, mordants, 331.
Titan red, 333.
,, yellow, 336.
Tiza, 415.
Toluene a source of artificial oil of bitter almonds, 241.
,, Boiling point of, 79.
,, sulphonic acids, 420.
Toluidine, 286.
Tolusafranine, 300.
Toluylene blue, 303, 314.
,, orange, 333.
,, red, 299.
Tonite, 405.
Top fermentation, 199; of wine, 206.
"Topping" with basic colours, 334.
Top yeast, 202.
Toughened glass, 156; Siemens', 156.
Tow, 262.
Tower, Gay-Lussac, 8; Glover, 7.
"Towers, Graduation," 21.
Train oil, 238.
Trass, 140.
Treacle, 164, 179; Analysis of, 164.

Triamidoazobenzene, Formula for, 275.
Triamidotriphenyl carbinol, 284.
Tricalcium saccharate, 174.
Trihydroxy-benzoic acid, 375.
Trihydroxytriphenylmethane dyestuffs, 291.
Trillo, 377.
Trimethylamine from beet juice, 165.
,, hydrochloride, 428.
Trimming hides, 384.
Trinidad asphaltum, 124.
Trinitrophenol, 273.
Triphenylmethanecarbinolorthocarboxylic acid, 293.
Triphenylmethane, Derivatives of, 286; Derivatives (dyestuffs), 283; Formation of, 286.
Triphenylrosaniline, 290.
Triple effect evaporators, 170.
Trisazo-compounds defined, 275.
Tropæolin O, 275.
,, Y, 275.
Tufa, Analysis of volcanic, 140.
Tumbling hides, 389.
Turkey-red dyeing, 282; Oils applied in, 282.
Turkey-red oil, 235; Manufacture of, 235.
Turkish boracite, 414.
Turmeric, 326.
Turnbull's blue, 357.
Turner's yellow, 361.
Turnips, Spirit from, 216.
Turpentine, 240; Adulterations of oil of, 240; American, 240; Commercial grades of, 240; Conifers, a source of, 240; French, 240; Oil of, 240; Oil of, for denaturing spirit, 219; Properties of, 240; Rectification of, 240; Russian, 240; Spirits of, 240; Yield of oil of, 240.
Turpentines, resins, caoutchouc, 240.
Turps, 240.
Tuscany boric acid, 414.
Tussur silk, 259.
Twill bags for sugar filtration, 178.

U

Ultramarine, 354; Analysis of, 356; Artificial, 354; as a colour corrective, 187, 267, 353; Bleaching of, by acids, 355; blue, 354; Direct process of making, 354; Direct process of production of blue, 355; for correcting yellow tints, 344; Green, 354; Green, converted into blue, 355; green, Difference of, from blue, 355; Hue of, 354; Knapp's theory of the colour of, 355; Potassium, 355; Silver, 355; Soda, 354; Sulphate, 354; Uses of, 356.
Umber, Burnt, 364; Raw, 364.
Umbers, 364.
Uncaria gambier, 377.
"Underback," 197.
Underburnt cement clinker, 139.
"Underlets," 196.
"Underproof," 218.
"Ungumming" silk, 265.
Unhairing hides, 382.
"Union goods," 335.
Union method of cleansing beer, 203.
Unorganised ferments, 189.
Unsaturated fatty acids, Oils containing, 226.
U.P., 218.
Uranium glass, 159.
,, oxide pigment for glass, 160.

V

Vacuum pan, 171, 172.
Valeric acid, 223.
Valonia, 377.
Valon's process, 65.
Valuation of ammoniacal liquor, 76.
,, coal gas, 67.
,, gas liquor, 76.
,, "manganese," 35.
Vanadium compounds, Application of, 311.
Vanillin in beet juice, 165.
Varnishes, 245; Denatured spirit for, 219; Drying of, 246; Manufacture of, 245; Nitrated cellulose, 246; Oil, 245; oil, Resins for, 245; resins and oils, 223; Resins for, 243; Spirit, 246; spirit, Solvents for, 246.
"Vat" dyeing with indigo, 322.
,, Copperas, for dyeing with indigo, 322.
,, Hyposulphite, for dyeing with indigo, 323.
,, Woad, for dyeing with indigo, 322.
Vats, Vinegar, 220.
Vaseline, 121; Decolorising, 433; from Russian petroleum, 123; Spurious, 121.

Vegetable black, 364.
,, fibres, Animal fibres distinguished from, 259.
,, oils, Winning and refining of, 228.
Vehicles for paints, 356.
Vellum, 391.
Venetian red, 363.
Verdigris, 359; "Distilled," 360.
Verditer, Blue, 358; Green, 360.
Vermilion, 362; Adulterations of, 362; Antimony, 363; Chinese process for making, 362; Dry method of making, 362; Dutch process for making, 362; Idrian process for making, 362; Wet method of making, 362.
Vermilionettes, 365.
Victoria blue, 290, 307.
Vinasse, 428.
Vinegar, 219; Ale, 221; Caramel for colouring, 182; Cider, 221; eel, 221; Factitious, from acetic acid, 222; fly, 221; from malt, 220; making, Conditions of, 221; Malt, 221; malt, Composition of, 221; Mother of, 219; Orleans process for making, 219; Perry, 221; process, Beech shavings for, 220; process, Quick, 220; process, Slow, 219; "Proof," 221; Sugar, 221; Sulphuric acid in, 221; Trade designation of quality of, 221; vats, 220; White malt, 222; wine, Composition of, 222.
Vines, Antiseptics for, 206.
Virgin oil, 231.
Viscosimetry, Standard of, 232.
Viscosity imparted to oils, 234.
,, Oils of high, 227.
Vitreous arsenic, 416.
Vitriol, Black, 424; Blue, 423; Brown oil of, 15.
Vitriol chamber, reactions in, 11, 12, 13.
Vitriol chambers, Acid "drips" in 14; "Curtains" of, 7; Lead for, 7; Saucers of, 7.
Vitriol, Concentration of, 15.
,, ,, in cast iron, 16.
,, ,, in glass stills, 15.
,, ,, lead pans, 15.
,, ,, platinum stills, 15.
,, Corrosion of platinum by, 15.
,, Gold-lined stills for, 16.
,, Green, 423.
Vitriol making, Causes of loss of nitre in, 13.
,, ,, Plant for, 5.
,, ,, Process of, 2.
,, ,, Nitric acid in, 14.
,, ,, Quantity of nitre used in, 13.
,, ,, Regulation of, by Alkali Act, 15.
,, ,, Water spray in, 11.
,, Nitrous, 13.
,, pans, Quality of lead for, 15.
,, Purification of, 16.
,, Raw materials for, 2.
,, "shales," 17.
,, "stone," 18.
,, "tar," 101.
,, ,, Rave's treatment of, 101.
,, White, 424.
Vitriols, 423.
Volcanic tufa, Analysis of, 140.
Vulcanisation of rubber, 244.
,, Sulphur chloride process for, 244.
Vulcanised caoutchouc, 243.
,, rubber, 243 (see also *Rubber*).
Vulcanite, 244.

W

Walnut oil, 226.
Warble marks, Prevention of, 372.
Wash, 391; Composition of whiskey, 211.
Washer, Gas, 64.
Washing soda, 29.
Wash, Spent, 214; as a fodder, 216.
Waste, alkali, Analysis of, 32.
,, ,, Sulphur recovery from, 32.
,, ,, Treatment of, 32.
,, Tank, 28, 32.
,, ,, Treatment of, 32.
Water, alkaline, Effect of, in brewing, 199.
,, Burton, 195.
,, "Burtonising," 195.
"Water-fall" malt screen, 191.
Water for black beer, 195.
Water for brewing, 194; Advantage of the presence of calcium sulphate in, 199; Analysis of, 195; Effect of sodium chloride in, 189.
Water for dyeing, 343.
,, for mild ale, 195.
,, for pale ale, 195.

Water for stout, 195.
,, for tanneries, 372.
,, gas, Energy absorbed in production of, 72.
,, ,, Manufacture of, 72.
,, glass, 141.
,, hard, Objections to, in tanneries, 373.
,, Influence of, on mashing and boiling in brewing, 199.
,, in soap, 248.
,, in wood, Percentage of, 88.
,, London deep-well, 195.
,, seals prevented from freezing, 256.
,, spray in vitriol making, 11.
,, tannin, 375.
Waterproofed matches, 412.
Waters rendered fit for brewing, 195.
Water-white kerosene, 121.
Wattle bark, 378.
Wax, Adulterations of, 239; Bleaching of, 239, 251; Chromic acid for bleaching, 239; for candles, 251; Japan, 227; Melting point of paraffin, 102; Myrtle, 227; Paraffin, 102; Paraffin, from petroleum, 121; Paraffin, in Russian petroleum, 123; Properties of, 239; Sealing, 242.
Waxes defined, 225.
,, Difference of, from fats, 225.
,, Hydrolysis of, 225.
,, Liquid, 228.
,, Solid, 228.
,, Winning of vegetable, 229.
Weed, Orchella, 326; Orchil, 326.
Weld, 326.
Weldon manganese recovery process, 37.
,, mud, Composition of, 38.
,, ,, for gas purification, 66.
,, process, Chemistry of, 38.
,, Péchiney process, Chlorine recovery by, 50.
,, process, Function of calcium chloride in, 38.
Welsbach burner, 70.
Wenham burner, 70.
West-Knight and Gall process, 79.
Wet method of making vermilion, 362.
Wetzel evaporators, 164.
Whale, Blubber of, 238.
,, oil, 228, 238; group, Oils of, 228.
Wheat starch, 185; Manufacture of, 185.
Whiskey, 210; Content of alcohol in, 211; Drying malt for, 210; Fermentation of wort for, 210; Fractionation of, 211; Furfural in, 212; Fusel oil in, 211; Irish, 210; Mashing malt for, 210; Maturing of, 212; New, 211; Scotch, 210; Still for, 211; stills, Frothing prevented in, by soap, 211; stills, Lactic acid from, 211; Use of sherry cask for maturing of, 212; wash, Composition of, 211; Wort for, 210.
White arsenic, 415; for curing hides, 372; Manufacture of, arsenic acid from, 416; Purification of, 416; Uses of, 416.
White galls, 374.
,, leather, 390.
White lead, 349; Adulterants of, 352; Analysis of sublimed, 352; Barytes in, 352; Caledonian, 353; Chamber method of making, 350; Clichy process of making, 351; Composition of, 352; Dutch process of making, 349; French process of making, 351; German method of making, 350; "Ground," 352; manufacture, Chemistry of, 350; Milner's process of making, 351; Precipitation processes of making, 351; Prevention of poisoning by, 352; Stack process of making, 349; "Sublimed," 352.
White pigments, 349.
,, ,, containing lead, 352.
,, sour, 266.
,, sugar, 180.
,, vitriol, 424.
,, wine, Vinegar from, 220.
,, Zinc, 353 (see also *Zinc white*).
Whitening of leather, 393.
Whitewash, 354.
Whiting, 354.
Wick, Function of candle, 250.
Wicks, Treatment of candle, 251.
"Wild" silks, 259.
Wine, Beech shavings for clarifying, 220; Bottom fermentation of, 206; Bouquet of, 207; Cause of colour in, 208; Coloured, 327; Crust of, 208; defined, 205; Effect of plaster of Paris upon fermentation of, 208; Index of genuine, 207; Influence of temperature on production of, 206; Top fermentation of, 206; Treatment of grapes for red, 206; Treatment of grapes for white,

206; Vinegar, 221; vinegar, Composition of, 222; White vinegar from, 220; Yield of brandy from, 209; Young, 206.
Wines, Analysis of, 207; Analysis of fortified, 208; Bouquet of, 208; Fortified, 207; Keeping properties of red, 207; Low, 211; Plastered, 208.
Wintergreen, Adulteration of oil of, 241; Artificial oil of, 241; Oil of, 241, 419.
Witherite, 430.
Witt's theory of dyestuffs, 273.
Woad, 319; vat for dyeing with indigo, 322.
Wood ashes as manure, 114; ashes, Potash from, 428; Bar, 325; Brazil, 325; Cam, 325; Carbonising, in kilns, 90; Carbonising, in retorts, 90; charcoal for purifying spirit, 216; Destructive distillation of, 88; distillation, Yield of acetic acid by, 95; distillation, Yield of products from, 92; Exothermic decomposition of, 96; Fustet, 325; gas, Analysis of, 95; Lima, 325; Manufacture of paper from, 345; naphtha, 93; naphtha, Denaturing alcohol by, 218; Peach, 325; Percentage of water in, 88.
Wood pulp, Calcium bisulphite for making, 347; Chemical, 345; Effect of light on mechanical, 345; Magnesium bisulphite for making, 347; Mechanical, 345; Sodium sulphide for making, 346; Sulphite process for making, 347; Yield of, 347.
Wood rendered fireproof, 142.
Wood, Santal, 325; Sapan, 325; spirit, 93; spirit, Composition of, 94; Staining, 423; tar, 92; tar creosote, 93; wool, 262; Yellow Brazilian, 325; Yield of charcoal from, 89, 90; Yield of oxalic acid from, 417.
Wool, Action of alkali on, 271; bleaching, 264; Cotton, 260; "Diseased," 257; Dyeing, with acid colours, 336; Dyeing, with basic colours, 336; Dyeing, with direct dyes, 335; Dyeing, with mordant colours, 337; fat, 258; fibre, Analysis of, 258; fibres, properties of, 259; fibres, Length of, 257; fibres, Specific gravity of, 259; Glass, 263; grease, 258; Hygroscopic character of, 258; Moisture in, 258; printing, 342; Raw, 258; Slag, 263; "Staple" of, 257; Structure of, 257; sweat, 258; washing, 258; Wood, 262; Yellowing of, by soap, 264.
Wormwood, 215.
Wort, 196; Analysis of, 198; Attenuation of, 199; boiling in brewing, 197; cooling in brewing, 198; Fermentation of, 199; for whiskey, 210; for whiskey, Fermentation of, 210; "Pitching," 199.

X

Xanthorhamnin, 326.
Xylene, Boiling point of, 79.
Xylidine, 286.

Y

Yaryan evaporator, 170.
Yeast, 200; Analysis of, 200; Analysis of ash of, 201; Bacteria in, 202; Bottom, 202; Characteristics of good, 202; Condition of must for rapid propagation of, 202; Endogenous division of, 200; Fission of, 200; for distilleries, 211; Gemmation of, 200; Moulds in, 202; Proportion of, used in brewing, 199; pure, Cultivation of, 203; reproduction of, Conditions influencing, 200; Top, 202.
Yeasts, 189.
Yellow, Alizarin, 338.
,, arsenic, 383.
,, colour imparted to margarine, 238.
,, colour of bleached cotton corrected, 267,
,, phosphorus, Properties of, 408.
,, pigments, 360.
,, prussiate of potash, 433.
,, tint of starch corrected, 187.
,, Titan, 336.
,, vegetable colours, 326.
,, wax from petroleum, 122.
,, wood, Brazilian, 325.
Yellowing of wool by soap, 264.
Yolk, 258; Potash from, 429.
Yolk of egg used in tanning, 390.
Yorkshire grease, 258.

Young and Beilby retort for shale distillation, 97, 99.
,, fustic, 325.
,, wine, 206.

Z

Zaffre, 357.
Zambesi blues, 333.
Zero point, Thermometers of constant, 160.
Zettlitz kaolin, 143.
Zinc chromate, 361.
,, dust as a discharge, 341.
,, oxide for hydrolysing fats, 253.
,, ,, Preparation of, 353.
,, sulphate, 424.
Zinc white, 353; Adulterations of, 353; discoloured by cadmium oxide, 353; discoloured by cadmium sulphide, 353; Orr's, 353; Purification of, 353.

BELL AND BAIN, LIMITED, PRINTERS, GLASGOW.

A SELECTION

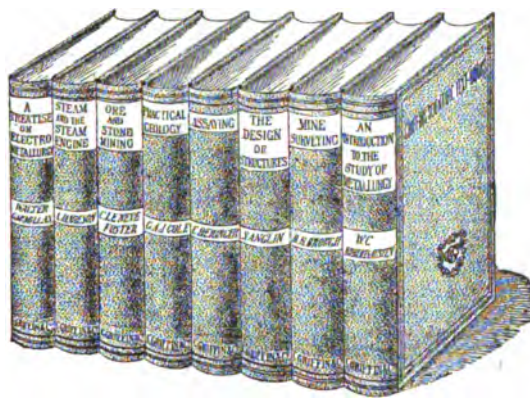
FROM THE

SCIENTIFIC AND TECHNICAL WORKS

PUBLISHED BY

CHARLES GRIFFIN & COMPANY, LIMITED.

(Being Sections 4-10 from Messrs. Griffin's "General Catalogue.")



MESSRS. CHARLES GRIFFIN & COMPANY'S PUBLICATIONS may be obtained through any Bookseller in the United Kingdom, or will be sent post free on receipt of remittance to cover published price. To prevent delay, Orders should be accompanied by a Remittance. Cheques and Postal Orders to be crossed "SMITH, PAYNE & SMITHS."

*** *For INDEX, see next page.*

☞ **MEDICAL, and GENERAL CATALOGUES forwarded Post-free on Application.**

LONDON:
EXETER STREET, STRAND.

INDEX.

PAGE

ALLINGHAM (W.), Navigation, 45, 47
—— Meteorology, ... 45
ANGLIN (S.), Design of Structures, . 26
BARKER (D. WILSON-), Navigation and Seamanship, ... 45, 47
BERINGER (J. J. & C.), Assaying, . 66
BILES (Prof. J. H.), Construction of Ships, ... 38
BLACKMORE (E.), British Mercantile Marine, ... 45-46
BLOUNT (B.) and BLOXAM (A. G.), Chemistry for Engineers and Manufacturers, ... 27, 71
BLYTH (A. Wynter), Foods and Poisons, 72
BORCHERS (Dr.), Electric Smelting, 67
BROTHERS (A.), Photography, . . 73
BROUGH (B. H.), Mine-Surveying, . 59
BROWNE (W. R.), Works by, . . 27
BRUCE (Robt.), Food Supply, . . 54
BUCK (R. C.), Algebra and Trigonometry, ... 45, 46
BUTTERFIELD (W. J. A.), Gas Manufacture, ... 74
CASTELL-EVANS (Prof.), Tables for Chemists, ... 75
COLE (Prof G. A. J.), Practical Geology, 53
—— Open Air Studies in Geology, . . 86
COLE (W. H.), Light Railways, . . 41
COX (S. H.), Prospecting for Minerals, 55
CRIMP (W. S.), Sewage Disposal Works, 28
DONKIN (Bryan), Gas and Oil Engines, 29
—— Efficiency of Steam Boilers, . . 29
DUERR (Geo.), Bleaching and Calico-Printing, ... 83
DUPRÉ & HAKE, Manual of Chemistry, 70
ETHERIDGE (R.), Stratigraphical Geology, ... 52
FIDLER (Prof.), Bridge-Construction, 30
FOSTER (Prof. C. le Neve), Ore and Stone Mining, ... 56
—— Elementary Mining, ... 56
GINSBURG (Dr.), Legal Duties of Shipmasters, ... 45, 49
GRIFFIN (J. J.), Chemical Recreations, 75
GRIFFIN'S Electrical Price-Book, . . 43
GRIFFIN'S ENGINEERING PUBLICATIONS, ... 25
GRIFFIN'S GEOLOGICAL and METALLURGICAL SERIES, . 51
GRIFFIN'S NAUTICAL SERIES, . . 45
GRIFFIN'S NEW LAND SERIES, 54
GRIFFIN'S CHEMICAL AND TECHNOLOGICAL PUBLICATIONS, ... 69
GURDEN (R.), Traverse Tables, . . 31
GUTTMANN (O.), Blasting, . . . 59
HARBORD (F. W.), Steel, ... 65
HUGHES (H. W.), Coal Mining, . . 57
HURST (Chas.), Valves and Valve-Gearing, ... 31
HURST (G. H.), Painters' Colours, . 76
—— Garment Dyeing and Cleaning . 83
JAMIESON (Prof.), MANUALS, Advanced and Elementary, ... 32
—— Steam Engine, ... 32
—— Applied Mechanics, ... 32
—— Magnetism and Electricity, . . 32
JENKINS (H. C.), Metallurgical Machinery, ... 62
JOHNSON (J. C. F.), Getting Gold, . 55
KNECHT & RAWSON, Dyeing, . . 81
LAFAR and SALTER, Technical Mycology, ... 79
LAWN (J. G.), Mine Accounts, . . 60

PAGE

LIVERSIDGE (J. G.), Engine-Room Practice, ... 34
MACKENZIE (T.), Mechanics for Sailors, ... 45, 48
M'MILLAN (W. G.), Electro-Metallurgy, 68
—— & BORCHERS, Electric Smelting, 67
MILLAR (W. J.), Latitude and Longitude: How to find them, . . . 45, 48
MUNRO & JAMIESON'S Electrical Pocket-Book, ... 43
MUNRO (Dr.), Agricultural Chemistry, 75
MUNRO (R. D.), Steam-Boilers, . . 33
—— Kitchen Boiler Explosions, . . 33
NYSTROM'S Pocket-Book for Engineers, 33
PEARCE (W. J.), Painting and Decorating, ... 77
PETTIGREW (W. F.), Manual of the Locomotive, ... 34
PHILLIPS & BAUERMAN, Metallurgy, 61
POYNTING (Prof.), Mean Density of the Earth, ... 44
PRAEGER (R. L.), Open Air Botany, . 86
RANKINE'S Applied Mechanics, . 35
—— Civil Engineering, ... 35
—— Machinery and Millwork, . . 35
—— Steam Engine & other Prime Movers, 35
—— Useful Rules and Tables, . . . 36
—— A Mechanical Text-Book, . . 36
—— Miscellaneous Scientific Papers, . 36
REDGRAVE (G. R.), Cements, . . 76
REDWOOD (Boverton), Petroleum, . . 58
REED (Sir E. J.), Stability of Ships, . 38
REID (Geo., M.D.), Practical Sanitation, 85
RICHMOND (H. D.), Dairy Chemistry, 25
RIDDELL (Dr. Scott), Ambulance Manual, ... 85
ROBERTS-AUSTEN (Prof.), Metallurgy and Alloys, ... 62, 63
ROBINSON (Prof.), Hydraulics, . . 37
ROSE (T. K.), Gold, Metallurgy of, . 64
ROTHWELL, (C. F. Seymour), Textile Printing, ... 82
SCHWACKHÖFER and BROWNE, Fuel and Water, ... 27
SEATON (A. E.), Marine Engineering, 39
SEATON & ROUNTHWAITE, Marine Engineers' Pocket-Book, . . . 39
SEELEY (Prof.), Physical Geology, . 52
SEXTON (Prof.), Elementary Metallurgy, ... 66
—— Quantitative & Qualitative Analysis, 70
SHELTON (W. V.), Mechanic's Guide, 36
SMITH, (Johnson), Shipmaster's Medical Help, ... 49
SMITH (Prof. R. H.), Calculus for Engineers, ... 40
—— Measurement Conversions, . . 40
SYKES (Dr. W. J.), Brewing, . . . 78
THOMSON & POYNTING (Profs.) Text-Book of Physics, ... 44
TRAILL (T. W.), Boilers, Land and Marine, ... 41
TURNER (Thos.), Iron, Metallurgy of, 65
WALTON (T.), Know Your Own Ship, 41, 50
WATKINSON (Prof. W. H.), Gas and Oil Engines, ... 42
WELLS (S. H.), Engineering Drawing, 42
WIGLEY (T. B.), Goldsmith and Jeweller's Art, ... 68
WRIGHT (Dr. Alder), The Threshold of Science, ... 80
—— Oils and Fats, Soaps and Candles, . 80
YEAMAN (C. H.), Elec. Measurements, 43
YEAR-BOOK of Scientific Societies, . 84

§§ 4-5. Griffin's Standard Publications

FOR

ENGINEERS, ELECTRICIANS, ARCHITECTS, BUILDERS, NAVAL CONSTRUCTORS, AND SURVEYORS.

		PAGE
Applied Mechanics,	RANKINE, BROWNE, JAMIESON,	35, 27, 32
Civil Engineering,	PROF. RANKINE,	35
Bridge-Construction,	PROF. FIDLER,	30
Design of Structures,	S. ANGLIN,	26
Sewage Disposal Works,	SANTO CRIMP,	28
Traverse Tables,	R. L. GURDEN,	31
Light Railways,	W. H. COLE,	41
Marine Engineering,	A. E. SEATON,	39
Engine-Room Practice,	J. G. LIVERSIDGE,	34
Design and Construction of Ships,	PROF. HARVARD BILES,	38
Stability of Ships,	SIR E. J. REED,	38
The Steam-Engine,	RANKINE, JAMIESON,	35, 32
The Locomotive,	W. F. PETTIGREW,	34
Valves and Valve-Gearing,	CHAS. HURST,	31
Gas, Oil, and Air-Engines,	BRYAN DONKIN,	29
Boilers: Construction,	T. W. TRAILL,	41
,, Management,	R. D. MUNRO,	33
,, Heat Efficiency,	BRYAN DONKIN,	29
Chemistry for Engineers,	BLOUNT & BLOXAM,	27
Fuel and Water (for Steam Users),	SCHWACKHÖFER AND BROWNE,	27
Machinery and Millwork,	PROF. RANKINE,	35
Hydraulic Machinery,	PROF. ROBINSON,	37
Metallurgical Machinery,	H. C. JENKINS,	62
Nautical Text-Books,	Ed. by CAPT. BLACKMORE,	45
Useful Rules and Tables for Engineers, &c.,	PROFS. RANKINE AND JAMIESON,	36
Electrical Pocket-Book,	MUNRO AND JAMIESON,	43
Electrical Price-Book,	H. J. DOWSING,	43
The Calculus for Engineers,	PROF. ROBT. H. SMITH,	40
Graphic Tables for Conversion of Measurements,	PROF. ROBT. H. SMITH,	40
Marine Engineers' Pocket-Book,	SEATON AND ROUNTHWAITE,	39
Nystrom's Pocket-Book,	DENNIS MARKS,	33

THE DESIGN OF STRUCTURES:

A Practical Treatise on the Building of Bridges, Roofs, &c.

BY S. ANGLIN, C.E.,

Master of Engineering, Royal University of Ireland, late Whitworth Scholar &c.

With very numerous Diagrams, Examples, and Tables.
Large Crown 8vo. Cloth.

SECOND EDITION, *Revised*. 16s.

The leading features in Mr. Anglin's carefully-planned "Design of Structures" may be briefly summarised as follows:—

1. It supplies the want, long felt among Students of Engineering and Architecture, of a concise Text-book on Structures, requiring on the part of the reader a knowledge of ELEMENTARY MATHEMATICS only.

2. The subject of GRAPHIC STATICS has only of recent years been generally applied in this country to determine the Stresses on Framed Structures; and in too many cases this is done without a knowledge of the principles upon which the science is founded. In Mr. Anglin's work the system is explained from FIRST PRINCIPLES, and the Student will find in it a valuable aid in determining the stresses on all irregularly-framed structures.

3. A large number of PRACTICAL EXAMPLES, such as occur in the every-day experience of the Engineer, are given and carefully worked out, some being solved both analytically and graphically, as a guide to the Student.

4. The chapters devoted to the practical side of the subject, the Strength of Joints, Punching, Drilling, Rivetting, and other processes connected with the manufacture of Bridges, Roofs, and Structural work generally, are the result of MANY YEARS' EXPERIENCE in the bridge-yard; and the information given on this branch of the subject will be found of great value to the practical bridge-builder.

"Students of Engineering will find this Text-Book INVALUABLE."—*Architect*

"The author has certainly succeeded in producing a THOROUGHLY PRACTICAL Text-Book."—*Builder*.

"We can unhesitatingly recommend this work not only to the Student, as the BEST TEXT-BOOK on the subject, but also to the professional engineer as an EXCEEDINGLY VALUABLE book of reference."—*Mechanical World*.

"This work can be CONFIDENTLY recommended to engineers. The author has wisely chosen to use as little of the higher mathematics as possible, and has thus made his book of REAL USE TO THE PRACTICAL ENGINEER. . . . After careful perusal, we have nothing but praise for the work."—*Nature*.

In Large 8vo. Handsome Cloth. 10s. 6d.

CHEMISTRY FOR ENGINEERS.

BY

BERTRAM BLOUNT, F.I.C., F.C.S., A.I.C.E., Consulting Chemist to the Crown Agents for the Colonies.

AND

A. G. BLOXAM, F.I.C., F.C.S., Consulting Chemist, Head of the Chemistry Department, Goldsmiths' Inst., New Cross.

GENERAL CONTENTS.—Introduction—Chemistry of the Chief Materials of Construction—Sources of Energy—Chemistry of Steam-raising—Chemistry of Lubrication and Lubricants—Metallurgical Processes used in the Winning and Manufacture of Metals.

"The authors have SUCCEEDED beyond all expectation, and have produced a work which should give FRESH POWER to the Engineer and Manufacturer."—*The Times.*

"PRACTICAL THROUGHOUT . . . AN ADMIRABLE TEXT-BOOK, useful not only to Students, but to ENGINEERS and MANAGERS OF WORKS in PREVENTING WASTE and IMPROVING PROCESSES."—*Scotsman.*

"A book worthy to take HIGH RANK . . . treatment of the subject of GASEOUS FUEL particularly good. . . . WATER GAS and its production clearly worked out. . . . We WARMLY RECOMMEND the work."—*Journal of Gas Lighting.*

For Companion Volume by the same Authors, "CHEMISTRY FOR MANUFACTURERS," see p. 71.

WORKS BY WALTER R. BROWNE, M.A., M.INST.C.E.,

Late Fellow of Trinity College, Cambridge.

THE STUDENT'S MECHANICS:

An Introduction to the Study of Force and Motion.

With Diagrams. Crown 8vo. Cloth, 4s. 6d.

"Clear in style and practical in method, 'THE STUDENT'S MECHANICS' is cordially to be commended from all points of view."—*Athenæum.*

FOUNDATIONS OF MECHANICS.

Papers reprinted from the *Engineer.* In Crown 8vo, 1s.

Demy 8vo, with Numerous Illustrations, 9s.

FUEL AND WATER:

A Manual for Users of Steam and Water.

BY PROF. FRANZ SCHWACKHÖFER OF VIENNA, AND WALTER R. BROWNE, M.A., C.E.,

GENERAL CONTENTS.—Heat and Combustion—Fuel, Varieties of—Firing Arrangements: Furnace, Flues, Chimney—The Boiler, Choice of—Varieties—Feed-water Heaters—Steam Pipes—Water: Composition, Purification—Prevention of Scale, &c., &c

"The Section on Heat is one of the best and most lucid ever written."—*Engineer.*

"Cannot fail to be valuable to thousands using steam power."—*Railway Engineer.*

SECOND EDITION, *Revised.* *Royal 8vo.* *With numerous Illustrations and 13 Lithographic Plates.* *Handsome Cloth.* *Price 30s.*

BRIDGE-CONSTRUCTION

(A PRACTICAL TREATISE ON):

Being a Text-Book on the Construction of Bridges in Iron and Steel.

FOR THE USE OF STUDENTS, DRAUGHTSMEN, AND ENGINEERS.

BY T. CLAXTON FIDLER, M. INST. C.E.,
Prof. of Engineering, University College, Dundee.

GENERAL CONTENTS.

PART I.—ELEMENTARY STATICS:—Definitions—The Opposition and Balance of Forces—Bending Strain—The Graphic Representation of Bending Moments.

PART II.—GENERAL PRINCIPLES OF BRIDGE-CONSTRUCTION:—The Comparative Anatomy of Bridges—Combined or Composite Bridges—Theoretical Weight of Bridges—On Deflection, or the Curve of a Bended Girder—Continuous Girders.

PART III.—THE STRENGTH OF MATERIALS:—Theoretical Strength of Columns—Design and Construction of Struts—Strength and Construction of Ties—Working Strength of Iron and Steel, and the Working Stress in Bridges—Wöhler's Experiments.

PART IV.—THE DESIGN OF BRIDGES IN DETAIL:—The Load on Bridges—Calculation of Stresses due to the Movable Load—Parallel Girders—Direct Calculation of the Weight of Metal—Parabolic Girders, Polygonal Trusses, and Curved Girders—Suspension Bridges and Arches: Flexible Construction—Rigid Construction—Bowstring Girders used as Arches or as Suspension Bridges—Rigid Arched Ribs or Suspension Ribs—Continuous Girders and Cantilever Bridges—The Niagara Bridge—The Forth Bridge—Wind-Pressure and Wind-Bracing: Modern Experiments.

"Mr. FIDLER'S SUCCESS arises from the combination of EXPERIENCE and SIMPLICITY OF TREATMENT displayed on every page. . . . Theory is kept in subordination to Practice, and his book is, therefore, as useful to girder-makers as to students of Bridge Construction."—*The Architect.*

"Of late years the American treatises on Practical and Applied Mechanics have taken the lead . . . since the opening up of a vast continent has given the American engineer a number of new bridge-problems to solve . . . but we look to the PRESENT TREATISE ON BRIDGE-CONSTRUCTION, and the Forth Bridge, to bring us to the front again."—*Engineer.*

"One of the VERY BEST RECENT WORKS on the Strength of Materials and its application to Bridge-Construction. . . Well repays a careful Study."—*Engineering.*

"AN INDISPENSABLE HANDBOOK for the practical Engineer."—*Nature.*

FOURTH EDITION. Folio, strongly half-bound, 21/.

TRAVERSE TABLES:

Computed to Four Places Decimals for every Minute of Angle up to 100 of Distance.

For the use of Surveyors and Engineers.

BY

RICHARD LLOYD GURDEN,

Authorised Surveyor for the Governments of New South Wales and Victoria.

*** *Published with Concurrence of the Surveyors-General for New South Wales and Victoria.*

"Those who have experience in exact SURVEY-WORK will best know how to appreciate the enormous amount of labour represented by this valuable book. The computations enable the user to ascertain the sines and cosines for a distance of twelve miles to within half an inch, and this BY REFERENCE TO BUT ONE TABLE, in place of the usual Fifteen minute computations required. This alone is evidence of the assistance which the Tables ensure to every user, and as every Surveyor in active practice has felt the want of such assistance, few knowing of their publication will remain without them."—*Engineer.*

In Large 8vo. With Numerous Illustrations. Price 7s. 6d.

VALVES AND VALVE-GEARING:

INCLUDING THE CORLISS VALVE AND TRIP GEARS.

BY

CHARLES HURST, Practical Draughtsman.

"CONCISE explanations illustrated by 115 VERY CLEAR DIAGRAMS and drawings and 4 folding-plates. . . . the book fulfils a VALUABLE function."—*Athenæum.*

"MR. HURST'S VALVES and VALVE-GEARING will prove a very valuable aid, and tend to the production of Engines of SCIENTIFIC DESIGN and ECONOMICAL WORKING. . . . Will be largely sought after by Students and Designers."—*Marine Engineer.*

"USEFUL and THOROUGHLY PRACTICAL. Will undoubtedly be found of GREAT VALUE to all concerned with the design of Valve-gearing."—*Mechanical World.*

"Almost EVERY TYPE of VALVE and its gearing is clearly set forth, and illustrated in such a WAY as to be READILY UNDERSTOOD and PRACTICALLY APPLIED by either the Engineer, Draughtsman, or Student. . . . Should prove both USEFUL and VALUABLE to all Engineers seeking for RELIABLE and CLEAR information on the subject. Its moderate price brings it within the reach of all."—*Industries and Iron.*

"Mr. HURST'S work is ADMIRABLY suited to the needs of the practical mechanic. . . . It is free from any elaborate theoretical discussion, and the explanations of the various types of valve-gear are accompanied by diagrams which render them EASILY UNDERSTOOD."—*The Scientific American.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

WORKS BY

ANDREW JAMIESON, M.INST.C.E., M.I.E.E., F.R.S.E.,

Professor of Electrical Engineering, The Glasgow and West of Scotland Technical College.

PROFESSOR JAMIESON'S ADVANCED MANUALS.

In Large Crown 8vo. Fully Illustrated.

1. STEAM AND STEAM-ENGINES (A Text-Book on). For the Use of Students preparing for Competitive Examinations. With over 200 Illustrations, Folding Plates, and Examination Papers. TWELFTH EDITION. Revised and Enlarged, 8/6.

"Professor Jamieson fascinates the reader by his CLEARNESS OF CONCEPTION AND SIMPLICITY OF EXPRESSION. His treatment recalls the lecturing of Faraday."—*Athenæum.*

"The BEST BOOK yet published for the use of Students."—*Engineer.*

"Undoubtedly the MOST VALUABLE AND MOST COMPLETE Hand-book on the subject that now exists."—*Marine Engineer.*

2. MAGNETISM AND ELECTRICITY (An Advanced Text-Book on). Specially arranged for Advanced and "Honours" Students.

3. APPLIED MECHANICS (An Advanced Text-Book on).

Vol. I.—Comprising Part I.: The Principle of Work and its applications; Part II.: Gearing. Price 7s. 6d. SECOND EDITION.

"FULLY MAINTAINS the reputation of the Author—more we cannot say."—*Pract. Engineer.*

Vol. II.—Comprising Parts III. to VI.: Motion and Energy; Graphic Statics; Strength of Materials; Hydraulics and Hydraulic Machinery. Price 7s. 6d.

"WELL AND LUCIDLY WRITTEN."—*The Engineer.*

PROFESSOR JAMIESON'S INTRODUCTORY MANUALS.

With numerous Illustrations and Examination Papers.

1. STEAM AND THE STEAM-ENGINE (Elementary Text-Book on). For First-Year Students. SIXTH EDITION. 3/6.

"Quite the RIGHT SORT OF BOOK."—*Engineer.*

"Should be in the hands of EVERY engineering apprentice."—*Practical Engineer*

2. MAGNETISM AND ELECTRICITY (Elementary Text-Book on). For First-Year Students. FOURTH EDITION. 3/6.

"A CAPITAL TEXT-BOOK . . . The diagrams are an important feature."—*Schoolmaster.*

"A THOROUGHLY TRUSTWORTHY Text-book. . . . Arrangement as good as well can be. . . . Diagrams are also excellent. . . . The subject throughout treated as an essentially PRACTICAL one, and very clear instructions given."—*Nature.*

3. APPLIED MECHANICS (Elementary Text-Book on). Specially arranged for First-Year Students. THIRD EDITION, Revised and Enlarged. 3/6.

"Nothing is taken for granted. . . . The work has VERY HIGH QUALITIES, which may be condensed into the one word 'CLEAR.'"—*Science and Art.*

A POCKET-BOOK of ELECTRICAL RULES and TABLES.

FOR THE USE OF ELECTRICIANS AND ENGINEERS.

Pocket Size. Leather, 8s. 6d. *Thirteenth Edition.*

SECOND EDITION. *Enlarged, and very fully Illustrated. Cloth,* 4s. 6d.

STEAM-BOILERS:

THEIR DEFECTS, MANAGEMENT, AND CONSTRUCTION.

BY R. D. MUNRO,

Chief Engineer of the Scottish Boiler Insurance and Engine Inspection Company.

GENERAL CONTENTS.—I. EXPLOSIONS caused (1) by Overheating of Plates—(2) By Defective and Overloaded Safety Valves—(3) By Corrosion, Internal or External—(4) By Defective Design and Construction (Unsupported Flue Tubes; Unstrengthened Manholes; Defective Staying; Strength of Rivetted Joints; Factor of Safety)—II. CONSTRUCTION OF VERTICAL BOILERS: Shells—Crown Plates and Uptake Tubes—Man-Holes, Mud-Holes, and Fire-Holes—Fireboxes—Mountings—Management—Cleaning—Table of Bursting Pressures of Steel Boilers—Table of Rivetted Joints—Specifications and Drawings of Lancashire Boiler for Working Pressures (*a*) 80 lbs.; (*b*) 200 lbs. per square inch respectively.

This work contains information of the first importance to every user of Steam-power. It is a PRACTICAL work written for PRACTICAL men, the language and rules being throughout of the simplest nature.

"A valuable companion for workmen and engineers engaged about Steam Boilers, ought to be carefully studied, and ALWAYS AT HAND."—*Coll. Guardian.*

"The book is VERY USEFUL, especially to steam users, artisans, and young engineers."—*Engineer.*

BY THE SAME AUTHOR.

KITCHEN BOILER EXPLOSIONS: Why they Occur, and How to Prevent their Occurrence. A Practical Handbook based on Actual Experiment. With Diagrams and Coloured Plate, Price 3s.

NYSTROM'S POCKET-BOOK OF MECHANICS AND ENGINEERING. Revised and Corrected by W. DENNIS MARKS, Ph.B., C.E. (YALE S.S.S.), Whitney Professor of Dynamical Engineering, University of Pennsylvania. Pocket Size. Leather, 15s. TWENTIETH EDITION, Revised and greatly enlarged.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Large 8vo., Handsome Cloth. With numerous Plates reduced from Working Drawings and Illustrations in the Text.

THE DESIGN AND CONSTRUCTION

OF

LOCOMOTIVE ENGINES.

WITH AN HISTORICAL INTRODUCTION.

A PRACTICAL TEXT-BOOK

For the Use of Engine Builders, Designers, and Draughtsmen, Railway Engineers, and Students.

BY

WILLIAM FRANK PETTIGREW, M.INST.C.E.

With a Section on American and Continental Engines.

BY

ALBERT F. RAVENSHEAR, B.Sc.,

Of Her Majesty's Patent Office.

Large Crown 8vo. With numerous Illustrations.

ENGINE-ROOM PRACTICE:

A HANDBOOK FOR

Engineers and Officers in the Royal Navy and Mercantile Marine:

INCLUDING THE MANAGEMENT OF THE MAIN AND AUXILIARY ENGINES ON BOARD SHIP.

BY

JOHN G. LIVERSIDGE,

Engineer, R.N., A.M.I.C.E., Instructor in Applied Mechanics at the Royal Naval College, Greenwich.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

WORKS BY

W. J. MACQUORN RANKINE, LL.D., F.R.S.,

Late Regius Professor of Civil Engineering in the University of Glasgow.

THOROUGHLY REVISED BY

W. J. MILLAR, C.E.,

Late Secretary to the Institute of Engineers and Shipbuilders in Scotland.

I. A MANUAL OF APPLIED MECHANICS:

Comprising the Principles of Statics and Cinematics, and Theory of Structures, Mechanism, and Machines. With Numerous Diagrams. Crown 8vo, cloth, 12s. 6d. FIFTEENTH EDITION.

II. A MANUAL OF CIVIL ENGINEERING:

Comprising Engineering Surveys, Earthwork, Foundations, Masonry, Carpentry, Metal Work, Roads, Railways, Canals, Rivers, Waterworks, Harbours, &c. With Numerous Tables and Illustrations. Crown 8vo, cloth, 16s. TWENTIETH EDITION.

III. A MANUAL OF MACHINERY AND MILLWORK:

Comprising the Geometry, Motions, Work, Strength, Construction, and Objects of Machines, &c. Illustrated with nearly 300 Woodcuts. Crown 8vo, cloth, 12s. 6d. SEVENTH EDITION.

IV. A MANUAL OF THE STEAM-ENGINE AND OTHER PRIME MOVERS:

With a Section on GAS, OIL, and AIR ENGINES. By BRYAN DONKIN, M.Inst.C.E. With Folding Plates and Numerous Illustrations. Crown 8vo, cloth, 12s. 6d. FOURTEENTH EDITION.

PROF. RANKINE'S WORKS—(*Continued*).

V. USEFUL RULES AND TABLES:

For Architects, Builders, Engineers, Founders, Mechanics, Shipbuilders, Surveyors, &c. With APPENDIX for the use of ELECTRICAL ENGINEERS. By Professor JAMIESON, F.R.S.E. SEVENTH EDITION. 10s. 6d.

VI. A MECHANICAL TEXT-BOOK:

A Practical and Simple Introduction to the Study of Mechanics. By Professor RANKINE and E. F. BAMBER, C.E. With Numerous Illustrations. Crown 8vo, cloth, 9s. FOURTH EDITION.

*** *The* "MECHANICAL TEXT-BOOK" *was designed by* Professor RANKINE *as an* INTRODUCTION *to the above Series of Manuals.*

VII. MISCELLANEOUS SCIENTIFIC PAPERS.

Royal 8vo. Cloth, 31s. 6d.

Part I. Papers relating to Temperature, Elasticity, and Expansion of Vapours, Liquids, and Solids. Part II. Papers on Energy and its Transformations. Part III. Papers on Wave-Forms, Propulsion of Vessels, &c.

With Memoir by Professor TAIT, M.A. Edited by W. J. MILLAR, C.E. With fine Portrait on Steel, Plates, and Diagrams.

"No more enduring Memorial of Professor Rankine could be devised than the publication of these papers in an accessible form. . . . The Collection is most valuable on account of the nature of his discoveries, and the beauty and completeness of his analysis. . . . The Volume exceeds in importance any work in the same department published in our time."—*Architect.*

SHELTON-BEY (W. Vincent, Foreman to the Imperial Ottoman Gun Factories, Constantinople):

THE MECHANIC'S GUIDE: A Hand-Book for Engineers and Artizans. With Copious Tables and Valuable Recipes for Practical Use. Illustrated. *Second Edition.* Crown 8vo. Cloth, 7/6.

SECOND EDITION, Revised and Enlarged.
In Large 8vo, Handsome cloth, 34s.

HYDRAULIC POWER
AND
HYDRAULIC MACHINERY.

BY

HENRY ROBINSON, M. INST. C.E., F.G.S.,

FELLOW OF KING'S COLLEGE, LONDON; PROF. OF CIVIL ENGINEERING, KING'S COLLEGE, ETC., ETC.

With numerous Woodcuts, and Sixty-nine Plates.

GENERAL CONTENTS.

Discharge through Orifices—Gauging Water by Weirs—Flow of Water through Pipes—The Accumulator—The Flow of Solids—Hydraulic Presses and Lifts—Cyclone Hydraulic Baling Press—Anderton Hydraulic Lift—Hydraulic Hoists (Lifts)—The Otis Elevator—Mersey Railway Lifts—City and South London Railway Lifts—North Hudson County Railway Elevator—Lifts for Subways—Hydraulic Ram—Pearsall's Hydraulic Engine—Pumping-Engines—Three-Cylinder Engines—Brotherhood Engine—Rigg's Hydraulic Engine—Hydraulic Capstans—Hydraulic Traversers—Movable Jigger Hoist—Hydraulic Waggon Drop—Hydraulic Jack—Duckham's Weighing Machine—Shop Tools—Tweddell's Hydraulic Rivetter—Hydraulic Jogglng Press—Tweddell's Punching and Shearing Machine—Flanging Machine—Hydraulic Centre Crane—Wrightson's Balance Crane—Hydraulic Power at the Forth Bridge—Cranes—Hydraulic Coal-Discharging Machines—Hydraulic Drill—Hydraulic Manhole Cutter—Hydraulic Drill at St. Gothard Tunnel—Motors with Variable Power—Hydraulic Machinery on Board Ship—Hydraulic Points and Crossings—Hydraulic Pile Driver—Hydraulic Pile Screwing Apparatus—Hydraulic Excavator—Ball's Pump Dredger—Hydraulic Power applied to Bridges—Dock-gate Machinery—Hydraulic Brake—Hydraulic Power applied to Gunnery—Centrifugal Pumps—Water Wheels—Turbines—Jet Propulsion—The Gerard-Barré Hydraulic Railway—Greathead's Injector Hydrant—Snell's Hydraulic Transport System—Greathead's Shield—Grain Elevator at Frankfort—Packing—Power Co-operation—Hull Hydraulic Power Company—London Hydraulic Power Company—Birmingham Hydraulic Power System—Niagara Falls—Cost of Hydraulic Power—Meters—Schönheyder's Pressure Regulator—Deacon's Waste-Water Meter.

"A Book of great Professional Usefulness."—*Iron.*

*** The SECOND EDITION of the above important work has been thoroughly revised and brought up to date. Many new full-page Plates have been added—the number being increased from 43 in the First Edition to 69 in the present.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

Royal 8vo. Handsome Cloth, 25s.

THE STABILITY OF SHIPS.

BY

SIR EDWARD J. REED, K.C.B., F.R.S., M.P.,

KNIGHT OF THE IMPERIAL ORDERS OF ST. STANILAUS OF RUSSIA; FRANCIS JOSEPH OF AUSTRIA; MEDJIDIE OF TURKEY; AND RISING SUN OF JAPAN; VICE-PRESIDENT OF THE INSTITUTION OF NAVAL ARCHITECTS.

With numerous Illustrations and Tables.

THIS work has been written for the purpose of placing in the hands of Naval Constructors, Shipbuilders, Officers of the Royal and Mercantile Marines, and all Students of Naval Science, a complete Treatise upon the Stability of Ships, and is the only work in the English Language dealing exhaustively with the subject.

In order to render the work complete for the purposes of the Shipbuilder, whether at home or abroad, the Methods of Calculation introduced by Mr. F. K. BARNES, Mr. GRAY, M. REECH, M. DAYMARD, and Mr. BENJAMIN, are all given separately, illustrated by Tables and worked-out examples. The book contains more than 200 Diagrams, and is illustrated by a large number of actual cases, derived from ships of all descriptions, but especially from ships of the Mercantile Marine.

The work will thus be found to constitute the most comprehensive and exhaustive Treatise hitherto presented to the Profession on the Science of the STABILITY OF SHIPS.

"Sir EDWARD REED'S 'STABILITY OF SHIPS' is INVALUABLE. In it the STUDENT, new to the subject, will find the path prepared for him, and all difficulties explained with the utmost care and accuracy; the SHIP-DRAUGHTSMAN will find all the methods of calculation at present in use fully explained and illustrated, and accompanied by the Tables and Forms employed; the SHIPOWNER will find the variations in the Stability of Ships due to differences in forms and dimensions fully discussed, and the devices by which the state of his ships under all conditions may be graphically represented and easily understood; the NAVAL ARCHITECT will find brought together and ready to his hand, a mass of information which he would otherwise have to seek in an almost endless variety of publications, and some of which he would possibly not be able to obtain at all elsewhere."—*Steamship.*

"This IMPORTANT AND VALUABLE WORK . . . cannot be too highly recommended to all connected with shipping interests."—*Iron.*

"This VERY IMPORTANT TREATISE, . . . the MOST INTELLIGIBLE, INSTRUCTIVE, and COMPLETE that has ever appeared."—*Nature.*

"The volume is an ESSENTIAL ONE for the shipbuilding profession."—*Westminster Review.*

COMPANION-WORK.

THE DESIGN AND CONSTRUCTION OF SHIPS.

By JOHN HARVARD BILES, M.Inst.N.A.,

Professor of Naval Architecture in the University of Glasgow.

In Active Preparation.

Thirteenth Edition. Price 21s.

Demy 8vo, Cloth. With Numerous Illustrations, reduced from Working Drawings.

A MANUAL OF

MARINE ENGINEERING:

COMPRISING THE DESIGNING, CONSTRUCTION, AND WORKING OF MARINE MACHINERY.

By A. E. SEATON, M. Inst. C. E., M. Inst. Mech. E., M.Inst.N.A.

GENERAL CONTENTS.

Part I.—Principles of Marine Propulsion.

Part II.—Principles of Steam Engineering.

Part III.—Details of Marine Engines: Design and Calculations for Cylinders, Pistons, Valves, Expansion Valves, &c.

Part IV.—Propellers.

Part V.—Boilers.

Part VI.—Miscellaneous.

*** The THIRTEENTH EDITION includes a Chapter on WATER-TUBE BOILERS, with Illustrations of the leading Types.

"In the three-fold capacity of enabling a Student to learn how to design, construct, and work a Marine Steam-Engine, Mr. Seaton's Manual has NO RIVAL."—*Times.*

"The important subject of Marine Engineering is here treated with the THOROUGHNESS that it requires. No department has escaped attention. . . . Gives the results of much close study and practical work."—*Engineering.*

"By far the BEST MANUAL in existence. . . . Gives a complete account of the methods of solving, with the utmost possible economy, the problems before the Marine Engineer."—*Athenæum.*

"The Student, Draughtsman, and Engineer will find this work the MOST VALUABLE HANDBOOK of Reference on the Marine Engine now in existence."—*Marine Engineer.*

FOURTH EDITION. With Diagrams. Pocket-Size, Leather. 8s. 6d.

A POCKET-BOOK OF

MARINE ENGINEERING RULES AND TABLES,

FOR THE USE OF

Marine Engineers, Naval Architects, Designers, Draughtsmen, Superintendents and Others.

BY

A. E. SEATON, M.I.C.E., M.I.Mech.E., M.I.N.A.,

AND

H. M. ROUNTHWAITE, M.I.Mech.E., M.I.N.A.

"ADMIRABLY FULFILS its purpose."—*Marine Engineer.*

WORKS BY PROF. ROBERT H. SMITH, Assoc.M.I.C.E.,

M.I.M.E., M.I.El.E., M.Fed.I.Mi.E., Whit. Sch., M.Ord.Meiji.

THE CALCULUS FOR ENGINEERS AND PHYSICISTS,

Applied to Technical Problems.

WITH EXTENSIVE

CLASSIFIED REFERENCE LIST OF INTEGRALS.

By PROF. ROBERT H. SMITH.

ASSISTED BY

R. F. MUIRHEAD, M.A., B.Sc.,

Formerly Clark Fellow of Glasgow University, and Lecturer on Mathematics at Mason College.

In Crown 8vo, extra, with Diagrams and Folding-Plate. 8s. 6d.

"PROF. R. H. SMITH'S book will be serviceable in rendering a hard road AS EASY AS PRACTICABLE for the non-mathematical Student and Engineer."—*Athenæum.*

"Interesting diagrams, with practical illustrations of actual occurrence, are to be found here in abundance. THE VERY COMPLETE CLASSIFIED REFERENCE TABLE will prove very useful in saving the time of those who want an integral in a hurry."—*The Engineer.*

MEASUREMENT CONVERSIONS

(English and French):

28 GRAPHIC TABLES OR DIAGRAMS.

Showing at a glance the MUTUAL CONVERSION of MEASUREMENTS in DIFFERENT UNITS

Of Lengths, Areas, Volumes, Weights, Stresses, Densities, Quantities of Work, Horse Powers, Temperatures, &c.

For the use of Engineers, Surveyors, Architects, and Contractors.

In 4to, Boards. 7s. 6d.

*** Prof. SMITH'S CONVERSION-TABLES form the most unique and comprehensive collection ever placed before the profession. By their use much time and labour will be saved, and the chances of error in calculation diminished. It is believed that henceforth no Engineer's Office will be considered complete without them.

"The work is INVALUABLE."—*Colliery Guardian.*

"Ought to be in EVERY office where even occasional conversions are required. . . . Prof. SMITH'S TABLES form very EXCELLENT CHECKS on results."—*Electrical Review.*

"Prof. Smith deserves the hearty thanks, not only of the ENGINEER, but of the COMMERCIAL WORLD, for having smoothed the way for the ADOPTION of the METRIC SYSTEM of MEASUREMENT, a subject which is now assuming great importance as a factor in maintaining our HOLD upon FOREIGN TRADE."—*The Machinery Market.*

THIRD EDITION, *Revised and Enlarged. Pocket-Size, Leather*, 12s 6d.: *also Larger Size for Office Use, Cloth*, 12s. 6d.

Boilers, Marine and Land:

THEIR CONSTRUCTION AND STRENGTH.

A HANDBOOK OF RULES, FORMULÆ, TABLES, &C., RELATIVE TO MATERIAL, SCANTLINGS, AND PRESSURES, SAFETY VALVES, SPRINGS, FITTINGS AND MOUNTINGS, &C.

FOR THE USE OF ENGINEERS, SURVEYORS, BOILER-MAKERS, AND STEAM USERS.

BY T. W. TRAILL, M. INST. C. E., F. E. R. N.,

Late Engineer Surveyor-in-Chief to the Board of Trade.

*** TO THE SECOND AND THIRD EDITIONS MANY NEW TABLES for PRESSURES up to 200 LBS. per SQUARE INCH have been added.

"THE MOST VALUABLE WORK on Boilers published in England."—*Shipping World.*

"Very unlike any of the numerous treatises on Boilers which have preceded it. . . . Really useful. . . . Contains an ENORMOUS QUANTITY OF INFORMATION arranged in a very convenient form. . . . Those who have to design boilers will find that they can settle the dimensions for any given pressure with almost no calculation with its aid. . . . A MOST USEFUL VOLUME . . . supplying information to be had nowhere else.'—*The Engineer.*

"As a handbook of rules, formulæ, tables, &c., relating to materials, scantlings, and pressures, this work will prove MOST USEFUL. The name of the Author is a sufficient guarantee for its accuracy. It will save engineers, inspectors, and draughtsmen a vast amount of calculation."—*Nature.*

"By such an authority cannot but prove a welcome addition to the literature of the subject. . . . We can strongly recommend it as being the MOST COMPLETE, eminently practical work on the subject."—*Marine Engineer.*

"To the engineer and practical boiler-maker it will prove INVALUABLE. The tables in all probability are the most exhaustive yet published . . . Certainly deserves a place on the shelf in the drawing office of every boiler shop."—*Practical Engineer.*

LIGHT RAILWAYS

AT HOME AND ABROAD.

BY WILLIAM HENRY COLE, M.INST.C.E.,

Late Deputy-Manager, Eastern Bengal and North-Western State Railways, P.W.D., India.

In Large 8vo. Handsome Cloth. With Illustrations.

[*Griffin's Engineering Series.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Crown 8vo, extra, with Numerous Illustrations. [*Shortly.*

GAS AND OIL ENGINES:

AN INTRODUCTORY TEXT-BOOK

On the Theory, Design, Construction, and Testing of Internal Combustion Engines without Boiler.

FOR THE USE OF STUDENTS.

BY

PROF. W. H. WATKINSON, WHIT. SCH., M.INST.MECH.E.,
Glasgow and West of Scotland Technical College.

Engineering Drawing and Design

(A TEXT-BOOK OF).

SECOND EDITION. In Two Parts, Published Separately.

VOL. I.—PRACTICAL GEOMETRY, PLANE, AND SOLID. 3s.
VOL. II.—MACHINE AND ENGINE DRAWING AND DESIGN. 4s. 6d.

BY

SIDNEY H. WELLS, WH.SC.,
A.M.INST.C.E., A.M.INST.MECH.E.,
Principal of, and Head of the Engineering Department in, the Battersea Polytechnic Institute; formerly of the Engineering Departments of the Yorkshire College, Leeds; and Dulwich College, London.

With many Illustrations, specially prepared for the Work, and numerous Examples, for the Use of Students in Technical Schools and Colleges.

"A THOROUGHLY USEFUL WORK, exceedingly well written. For the many Examples and Questions we have nothing but praise."—*Nature.*

"A CAPITAL TEXT-BOOK, arranged on an EXCELLENT SYSTEM, calculated to give an intelligent grasp of the subject, and not the mere faculty of mechanical copying. . . . Mr. Wells shows how to make COMPLETE WORKING-DRAWINGS, discussing fully each step in the design."—*Electrical Review.*

"The first book leads EASILY and NATURALLY towards the second, where the technical pupil is brought into contact with large and more complex designs."—*The Schoolmaster.*

MUNRO & JAMIESON'S ELECTRICAL POCKET-BOOK.

THIRTEENTH EDITION, Revised and Enlarged.

A POCKET-BOOK
OF
ELECTRICAL RULES & TABLES

FOR THE USE OF ELECTRICIANS AND ENGINEERS.

BY JOHN MUNRO, C.E., & PROF. JAMIESON, M.INST.C.E., F.R.S.E.

With Numerous Diagrams. Pocket Size. Leather, 8s. 6d.

GENERAL CONTENTS.

UNITS OF MEASUREMENT.	ELECTRO-METALLURGY.
MEASURES.	BATTERIES.
TESTING.	DYNAMOS AND MOTORS.
CONDUCTORS.	TRANSFORMERS.
DIELECTRICS.	ELECTRIC LIGHTING.
SUBMARINE CABLES.	MISCELLANEOUS.
TELEGRAPHY.	LOGARITHMS.
ELECTRO-CHEMISTRY.	APPENDICES.

"WONDERFULLY PERFECT. . . . Worthy of the highest commendation we can give it."—*Electrician.*

"The STERLING VALUE of Messrs. MUNRO and JAMIESON'S POCKET-BOOK."—*Electrical Review.*

Electrical Measurements & Instruments.

A Practical Hand-book of Testing for the Electrical Engineer.

BY CHARLES H. YEAMAN,

Assoc. Inst. E.E., formerly Electrical Engineer to the Corporation of Liverpool.

SECOND EDITION, 8s. 6d. Leather, for the Pocket, 8s. 6d.

GRIFFIN'S ELECTRICAL PRICE-BOOK.

For Electrical, Civil, Marine, and Borough Engineers, Local Authorities, Architects, Railway Contractors, &c., &c.

EDITED BY H. J. DOWSING,

Member of the Institution of Electrical Engineers; of the Society of Arts; of the London Chamber of Commerce, &c.

"The ELECTRICAL PRICE-BOOK REMOVES ALL MYSTERY about the cost of Electrical Power. By its aid the EXPENSE that will be entailed by utilising electricity on a large or small scale can be discovered."—*Architect.*

"The value of this Electrical Price-Book CANNOT BE OVER-ESTIMATED. . . . Will save time and trouble both to the engineer and the business man."—*Machinery.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

By PROFESSORS J. J. THOMSON & POYNTING.

In Large 8vo. Fully Illustrated.

A TEXT-BOOK OF PHYSICS:

COMPRISING

PROPERTIES OF MATTER; SOUND; HEAT; MAGNETISM AND ELECTRICITY; AND LIGHT.

BY

J. H. POYNTING,
Sc.D., F.R.S.,
Late Fellow of Trinity College, Cambridge; Professor of Physics, Mason College, Birmingham.

AND

J. J. THOMSON,
M.A., F.R.S.,
Fellow of Trinity College, Cambridge; Prof. of Experimental Physics in the University of Cambridge.

*** *Publishers' Note.*—It is intended that this IMPORTANT and LONG-EXPECTED TREATISE shall be issued in separate Volumes, each complete in itself, and published at regular intervals, beginning with SOUND, now at Press.

In large 8vo, with Bibliography, Illustrations in the Text, and seven Lithographed Plates. 12s. 6d.

THE MEAN DENSITY OF THE EARTH:

An Essay to which the Adams Prize was adjudged in 1893 in the University of Cambridge.

BY

J. H. POYNTING, Sc.D., F.R.S.,

Late Fellow of Trinity College, Cambridge; Professor of Physics, Mason College, Birmingham.

"An account of this subject cannot fail to be of GREAT and GENERAL INTEREST to the scientific mind. Especially is this the case when the account is given by one who has contributed so considerably as has Prof. Poynting to our present state of knowledge with respect to a very difficult subject. . . . Remarkably has Newton's estimate been verified by Prof. Poynting."—*Athenæum.*

---

§6. GRIFFIN'S NAUTICAL SERIES.

EDITED BY EDW. BLACKMORE,
Master Mariner, First Class Trinity House Certificate, Assoc. Inst. N.A.;
AND WRITTEN, MAINLY, by SAILORS for SAILORS.

"This ADMIRABLE SERIES."—*Fairplay.* "A VERY USEFUL SERIES."—*Nature.*
"The volumes of MESSRS. GRIFFIN'S NAUTICAL SERIES may well and profitably be read by ALL interested in our NATIONAL MARITIME PROGRESS."—*Marine Engineer.*
"EVERY SHIP should have the WHOLE SERIES as a REFERENCE LIBRARY. HANDSOMELY BOUND, CLEARLY PRINTED and ILLUSTRATED."—*Liverpool Journ. of Commerce.*

The Legal Duties of Shipmasters. By BENEDICT WM. GINSBURG, M.A., LL.D., of the Inner Temple and Northern Circuit: Barrister-at-Law. Price 4s. 6d. Postage 4d. [*Just Published.*

The British Mercantile Marine: An Historical Sketch of its Rise and Development. By the EDITOR, CAPT. BLACKMORE. 3s. 6d. Postage 4d.
"This ADMIRABLE book . . . TEEMS with useful information. Should be in the hands of every Sailor."—*Western Morning News.*

Elementary Seamanship. By D. WILSON-BARKER, Master Mariner, F.R.S.E., F.R.G.S. With numerous Plates, two in Colours, and Frontispiece. 5s. Postage 4d.
"This ADMIRABLE MANUAL, by CAPT. WILSON BARKER, of the 'Worcester,' seems to us PERFECTLY DESIGNED."—*Athenæum.*

Know Your Own Ship: A Simple Explanation of the Stability, Construction, Tonnage, and Freeboard of Ships. By THOS. WALTON, Naval Architect. With numerous Illustrations. THIRD EDITION. 5s. Postage 4d.
"MR. WALTON'S book will be found VERY USEFUL."—*The Engineer.*

The Construction and Maintenance of Vessels built of Steel. By THOS. WALTON, Naval Architect. [*Shortly.*

Navigation: Theoretical and Practical. By D. WILSON-BARKER, Master Mariner, &c., and WILLIAM ALLINGHAM. 3s. 6d. Postage 3d.
"PRECISELY the kind of work required for the New Certificates of competency. Candidates will find it INVALUABLE."—*Dundee Advertiser.*

Latitude and Longitude: How to find them. By W. J. MILLAR, C.E., late Sec. to the Inst. of Engineers and Shipbuilders in Scotland. 2s. Postage 3d.
"Cannot but prove an acquisition to those studying Navigation."—*Marine Engineer.*

Practical Mechanics: Applied to the requirements of the Sailor. By THOS. MACKENZIE, Master Mariner, F.R.A.S. 3s. 6d. Postage 3d.
"WELL WORTH the money . . . EXCEEDINGLY HELPFUL."—*Shipping World.*

Ocean Meteorology: For Officers of the Merchant Navy. By WILLIAM ALLINGHAM, First Class Honours, Navigation, Science and Art Department. [*Shortly.*

Trigonometry: For the Young Sailor, &c. By RICH. C. BUCK, of the Thames Nautical Training College, H.M.S. "Worcester." Price 3s. 6d. Postage 3d.
"This EMINENTLY PRACTICAL and RELIABLE volume."—*Schoolmaster.*

Practical Algebra. By RICH. C. BUCK. [*Shortly.*

A Medical and Surgical Help for Shipmasters. Including 'First Aid at Sea. By WM. JOHNSON SMITH, F.R.C.S., Principal Medical Officer, Seaman's Hospital, Greenwich. 6s. Postage 4d.
"SOUND, JUDICIOUS, REALLY HELPFUL."—*The Lancet.*

GRIFFIN'S NAUTICAL SERIES.

Price 3s. 6d. Post-free.

THE

British Mercantile Marine.

BY EDWARD BLACKMORE,

MASTER MARINER; ASSOCIATE OF THE INSTITUTION OF NAVAL ARCHITECTS; MEMBER OF THE INSTITUTION OF ENGINEERS AND SHIPBUILDERS IN SCOTLAND; EDITOR OF GRIFFIN'S "NAUTICAL SERIES."

GENERAL CONTENTS.—HISTORICAL: From Early Times to 1486—Progress under Henry VIII.—To Death of Mary—During Elizabeth's Reign—Up to the Reign of William III.—The 18th and 19th Centuries—Institution of Examinations—Rise and Progress of Steam Propulsion—Development of Free Trade—Shipping Legislation, 1862 to 1875—"Locksley Hall" Case—Shipmasters' Societies—Loading of Ships—Shipping Legislation, 1884 to 1894—Statistics of Shipping. THE PERSONNEL: Shipowners—Officers—Mariners—Duties and Present Position. EDUCATION: A Seaman's Education: what it should be—Present Means of Education—Hints. DISCIPLINE AND DUTY—Postscript—The Serious Decrease in the Number of British Seamen, a Matter demanding the Attention of the Nation.

"INTERESTING and INSTRUCTIVE . . . may be read WITH PROFIT and ENJOYMENT."—*Glasgow Herald.*

"EVERY BRANCH of the subject is dealt with in a way which shows that the writer 'knows the ropes' familiarly."—*Scotsman.*

"This ADMIRABLE book . . . TEEMS with useful information—Should be in the hands of every Sailor."—*Western Morning News.*

WORKS BY RICHARD C. BUCK,

of the Thames Nautical Training College, H.M.S. 'Worcester.'

1. A Manual of Trigonometry:

With Diagrams, Examples, and Exercises. Post-free 3s. 6d.

*** Mr. Buck's Text-Book has been SPECIALLY PREPARED with a view to the New Examinations of the Board of Trade, in which Trigonometry is an obligatory subject.

"This EMINENTLY PRACTICAL and RELIABLE VOLUME."—*Schoolmaster.*

2. A Manual of Algebra.

*** These elementary works on ALGEBRA and TRIGONOMETRY are written specially for those who will have little opportunity of consulting a Teacher. They are books for "SELF-HELP." All but the simplest explanations have, therefore, been avoided, and ANSWERS to the Exercises are given. Any person may readily, by careful study, become master of their contents, and thus lay the foundation for a further mathematical course, if desired. It is hoped that to the younger Officers of our Mercantile Marine they will be found decidedly serviceable. The Examples and Exercises are taken from the Examination Papers set for the Cadets of the "Worcester."

*** For complete List of GRIFFIN'S NAUTICAL SERIES, see p. 45.

GRIFFIN'S NAUTICAL SERIES.

Price 5s. Post-free.

A MANUAL OF

ELEMENTARY SEAMANSHIP.

BY

D. WILSON-BARKER, MASTER MARINER; F.R.S.E., F.R.G.S., &c., &c.;
YOUNGER BROTHER OF THE TRINITY HOUSE.

With Frontispiece, Twelve Plates (Two in Colours), and Illustrations in the Text.

GENERAL CONTENTS.—The Building of a Ship; Parts of Hull, Masts, &c.—Ropes, Knots, Splicing, &c.—Gear, Lead and Log, &c.—Rigging, Anchors—Sailmaking—The Sails, &c.—Handling of Boats under Sail—Signals and Signalling—Rule of the Road—Keeping and Relieving Watch—Points of Etiquette—Glossary of Sea Terms and Phrases—Index.

*** The volume contains the NEW RULES OF THE ROAD.

"This ADMIRABLE MANUAL, by CAPT. WILSON-BARKER of the "Worcester," seems to us PERFECTLY DESIGNED, and holds its place excellently in 'GRIFFIN'S NAUTICAL SERIES.' . . . Although intended for those who are to become Officers of the Merchant Navy, it will be found useful by ALL YACHTSMEN."—*Athenæum.*

"Five shillings will be WELL SPENT on this little book. CAPT. WILSON-BARKER knows from experience what a young man wants at the outset of his career."—*The Engineer.*

Price 3s. 6d. Post-free.

NAVIGATION:

PRACTICAL AND THEORETICAL.

BY DAVID WILSON-BARKER, R.N.R., F.R.S.E., &c., &c.,

AND

WILLIAM ALLINGHAM,

FIRST-CLASS HONOURS, NAVIGATION, SCIENCE AND ART DEPARTMENT.

With Numerous Illustrations and Examination Questions.

GENERAL CONTENTS.—Definitions—Latitude and Longitude—Instruments of Navigation—Correction of Courses—Plane Sailing—Traverse Sailing—Day's Work—Parallel Sailing—Middle Latitude Sailing—Mercator's Chart—Mercator Sailing—Current Sailing—Position by Bearings—Great Circle Sailing—The Tides—Questions—Appendix: Compass Error—Numerous Useful Hints, &c.—Index.

"PRECISELY the kind of work required for the New Certificates of competency in grades from Second Mate to extra Master. . . . Candidates will find it INVALUABLE."—*Dundee Advertiser.*

"A CAPITAL LITTLE BOOK . . . specially adapted to the New Examinations. The Authors are CAPT. WILSON-BARKER (Captain-Superintendent of the Nautical College, H.M.S. "Worcester," who has had great experience in the highest problems of Navigation), and MR. ALLINGHAM, a well-known writer on the Science of Navigation and Nautical Astronomy."—*Shipping World.*

*** For complete List of GRIFFIN'S NAUTICAL SERIES, see p. 45.

GRIFFIN'S NAUTICAL SERIES.

Crown 8vo, with Numerous Illustrations. Handsome Cloth. 3s. 6d

Practical Mechanics:

Applied to the Requirements of the Sailor.

BY THOS. MACKENZIE,

Master Mariner, F.R.A.S.

GENERAL CONTENTS.—Resolution and Composition of Forces—Work done by Machines and Living Agents—The Mechanical Powers: The Lever; Derricks as Bent Levers—The Wheel and Axle: Windlass; Ship's Capstan; Crab Winch—Tackles: the "Old Man"—The Inclined Plane; the Screw—The Centre of Gravity of a Ship and Cargo—Relative Strength of Rope: Steel Wire, Manilla, Hemp, Coir—Derricks and Shears—Calculation of the Cross-breaking Strain of Fir Spar—Centre of Effort of Sails—Hydrostatics: the Diving-bell; Stability of Floating Bodies; the Ship's Pump, &c.

"THIS EXCELLENT BOOK . . . contains a LARGE AMOUNT of information."—*Nature.*

"WELL WORTH the money . . . will be found EXCEEDINGLY HELPFUL."—*Shipping World.*

"NO SHIPS' OFFICERS' BOOKCASE will henceforth be complete without CAPTAIN MACKENZIE'S 'PRACTICAL MECHANICS.' Notwithstanding my many years' experience at sea, it has told me *how much more there is to acquire.*"—(Letter to the Publishers from a Master Mariner).

"I must express my thanks to you for the labour and care you have taken in 'PRACTICAL MECHANICS.' . . . IT IS A LIFE'S EXPERIENCE. . . . What an amount we frequently see wasted by rigging purchases without reason and accidents to spars, &c., &c.! 'PRACTICAL MECHANICS' WOULD SAVE ALL THIS."—(Letter to the Author from another Master Mariner).

Crown 8vo, with Diagrams. 2s.

Latitude and Longitude:

How to Find them.

BY W. J. MILLAR, C.E.,

Late Secretary to the Inst. of Engineers and Shipbuilders in Scotland.

"CONCISELY and CLEARLY WRITTEN . . . cannot but prove an acquisition to those studying Navigation."—*Marine Engineer.*

"Young Seamen will find it HANDY and USEFUL, SIMPLE and CLEAR."—*The Engineer.*

*** For Complete List of GRIFFIN'S NAUTICAL SERIES, see p. 45.

GRIFFIN'S NAUTICAL SERIES.

In Crown 8vo. Handsome Cloth. 4s. 6d.

THE LEGAL DUTIES OF SHIPMASTERS.

BY

BENEDICT WM. GINSBURG, M.A., LL.D. (CANTAB.),
Of the Inner Temple and Northern Circuit; Barrister-at-Law.

General Contents.—The Qualification for the Position of Shipmaster—The Contract with the Shipowner—The Master's Duty in respect of the Crew: Engagement; Apprentices; Discipline; Provisions, Accommodation, and Medical Comforts; Payment of Wages and Discharge—The Master's Duty in respect of the Passengers—The Master's Financial Responsibilities—The Master's Duty in respect of the Cargo—The Master's Duty in Case of Casualty—The Master's Duty to certain Public Authorities—The Master's Duty in relation to Pilots, Signals, Flags, and Light Dues—The Master's Duty upon Arrival at the Port of Discharge—Appendices relative to certain Legal Matters: Board of Trade Certificates, Dietary Scales, Stowage of Grain Cargoes, Load Line Regulations, Life-saving Appliances, Carriage of Cattle at Sea, &c., &c.—Copious Index.

"No intelligent Master should fail to add this to his list of useful and necessary books. The price (4s. 6d.) cannot be quoted as an excuse for non-possession, and a few lines of it may SAVE A LAWYER'S FEE, BESIDES ENDLESS WORRY."—*Liverpool Journal of Commerce.*

"SENSIBLE, plainly written, in CLEAR and NON-TECHNICAL LANGUAGE, and will be found of MUCH SERVICE by the Shipmaster."—*British Trade Review.*

FIRST AID AT SEA.

With Coloured Plates and Numerous Illustrations. 6s.

A MEDICAL AND SURGICAL HELP
FOR SHIPMASTERS AND OFFICERS
IN THE MERCHANT NAVY.

BY

WM. JOHNSON SMITH, F.R.C.S.,
Principal Medical Officer, Seamen's Hospital, Greenwich.

*** The attention of all interested in our Merchant Navy is requested to this exceedingly useful and valuable work. It is needless to say that it is the outcome of many years PRACTICAL EXPERIENCE amongst Seamen.

"SOUND, JUDICIOUS, REALLY HELPFUL."—*The Lancet.*

OCEAN METEOROLOGY
FOR OFFICERS OF THE MERCHANT NAVY.

BY

WILLIAM ALLINGHAM,
Joint-Author of "Navigation, Theoretical and Practical."

*** For Complete List of GRIFFIN'S NAUTICAL SERIES, see p. 45.

LONDON: CHARLES GRIFFIN & CO., LIM.TED, EXETER STREET, STRAND.

GRIFFIN'S NAUTICAL SERIES.

THIRD EDITION. *With Numerous Illustrations. Handsome Cloth. 5s.*

KNOW YOUR OWN SHIP.

BY THOMAS WALTON, NAVAL ARCHITECT.

SPECIALLY ARRANGED TO SUIT THE REQUIREMENTS OF SHIPS' OFFICERS, SHIPOWNERS, SUPERINTENDENTS, DRAUGHTSMEN, ENGINEERS, AND OTHERS.

This work explains, in a simple manner, such important subjects as:—

Displacement, Deadweight, Tonnage, Freeboard, Moments, Buoyancy, Strain, Structure, Stability, Rolling, Ballasting, Loading, Shifting Cargoes, Admission of Water, Sail Area, &c., &c.

"The little book will be found EXCEEDINGLY HANDY by most officers and officials connected with shipping. . . . Mr. Walton's work will obtain LASTING SUCCESS, because of its unique fitness for those for whom it has been written."—*Shipping World.*

"An EXCELLENT WORK, full of solid instruction and INVALUABLE to every officer of the Mercantile Marine who has his profession at heart."—*Shipping.*

"Not one of the 242 pages could well be spared. It will admirably fulfil its purpose . . . useful to ship owners, ship superintendents, ship draughtsmen, and all interested in shipping."—*Liverpool Journal of Commerce.*

"A mass of VERY USEFUL INFORMATION, accompanied by diagrams and illustrations, is given in a compact form."—*Fairplay.*

"A large amount of MOST USEFUL INFORMATION is given in the volume. The book is certain to be of great service to those who desire to be thoroughly grounded in the subject of which it treats."—*Steamship.*

"We have found no one statement that we could have wished differently expressed. The matter has, so far as clearness allows, been admirably condensed, and is simple enough to be understood by every seaman."—*Marine Engineer.*

BY THE SAME AUTHOR.

In Preparation.

THE CONSTRUCTION AND MAINTENANCE OF VESSELS BUILT OF STEEL.

*** For Complete List of GRIFFIN'S NAUTICAL SERIES, see p. 45.

§§ 7-8. Griffin's Geological, Prospecting, Mining, and Metallurgical Publications.

Handsome Cloth. Fully Illustrated. Post Free.

		PRICE
Geology, Stratigraphical,	R. ETHERIDGE, F.R.S.,	34/
,, Physical,	PROF. H. G. SEELEY,	18/
,, Practical Aids, 3rd Ed.,	PROF. GRENVILLE COLE,	10/6
,, Open Air Studies,	,, ,,	8/6
Griffin's "New Land" Series for Prospectors,	Ed. by PROF. COLE,	...
1. Prospecting for Minerals,	S. HERBERT COX, A.R.S.M.,	5/
2. Food Supply,	ROBT. BRUCE,	4/6
3. Building Construction,	PROF. JAS. LYON,	...
Ore and Stone Mining, 2nd Ed.,	PROF. LE NEVE FOSTER,	34/
Coal Mining, 3rd Ed.,	H. W. HUGHES, F.G.S.,	18/
Petroleum,	REDWOOD AND HOLLOWAY,	45/
Mine-Surveying, 6th Ed.,	BENNETT H. BROUGH, A.R.S.M.,	7/6
Blasting and Explosives,	O. GUTTMANN, A.M.I.C.E.,	10/6
Mine Accounts,	PROF. J. G. LAWN,	10/6
Metallurgy (General Treatise on), 3rd Ed.,	PHILLIPS AND BAUERMAN,	36/
,, (Elementary),	PROF. HUMBOLDT SEXTON,	6/
Assaying, 4th Ed.,	J. J. & C. BERINGER,	10/6
Griffin's Metallurgical Series	Ed. by PROF. ROBERTS-AUSTEN, C.B., F.R.S.,	...
1. Introduction to Metallurgy, 4th Ed.,	PROF. ROBERTS-AUSTEN,	15/
2. Gold, Metallurgy of, 3rd Ed.,	DR. KIRKE ROSE, A.R.S.M.,	21/
3. Iron, Metallurgy of,	THOS. TURNER, A.R.S.M.,	16/
4. Steel, ,,	F. W. HARBORD, A.R.S.M.,	...
5. Silver and Lead, ,,	H. F. COLLINS, A.R.S.M.,	...
6. Metallurgical Machinery,	H. C. JENKINS, A.R.S.M.,	...
Getting Gold, 2nd Ed.,	J. C. F. JOHNSON, F.G.S.,	3/6
Electric Smelting and Refining,	BORCHERS AND MCMILLAN,	21/
Electro-Metallurgy,	W. G. MCMILLAN, F.I.C.,	10/6
Goldsmith and Jeweller's Art,	THOS. B. WIGLEY,	...

Demy 8vo, Handsome cloth, 18s.

Physical Geology and Palæontology,

ON THE BASIS OF PHILLIPS.

BY

HARRY GOVIER SEELEY, F.R.S.,

PROFESSOR OF GEOGRAPHY IN KING'S COLLEGE, LONDON.

With Frontispiece in Chromo-Lithography, and Illustrations.

"It is impossible to praise too highly the research which PROFESSOR SEELEY'S 'PHYSICAL GEOLOGY' evidences. IT IS FAR MORE THAN A TEXT-BOOK—it is a DIRECTORY to the Student in prosecuting his researches."—*Presidential Address to the Geological Society*, 1885, *by Rev. Prof. Bonney D.Sc., LL.D., F.R.S.*

"PROFESSOR SEELEY maintains in his 'PHYSICAL GEOLOGY' the high reputation he already deservedly bears as a Teacher."—*Dr. Henry Woodward, F.R.S., in the "Geological Magazine."*

"PROFESSOR SEELEY'S work includes one of the most satisfactory Treatises on Lithology in the English language. . . . So much that is not accessible in other works is presented in this volume, that no Student of Geology can afford to be without it."—*American Journal of Engineering.*

Demy 8vo, Handsome cloth, 34s.

Stratigraphical Geology & Palæontology,

ON THE BASIS OF PHILLIPS.

BY

ROBERT ETHERIDGE, F.R.S.,

OF THE NATURAL HIST. DEPARTMENT, BRITISH MUSEUM, LATE PALÆONTOLOGIST TO THE GEOLOGICAL SURVEY OF GREAT BRITAIN, PAST PRESIDENT OF THE GEOLOGICAL SOCIETY, ETC.

With Map, Numerous Tables, and Thirty-six Plates.

"No such compendium of geological knowledge has ever been brought together before."—*Westminster Review.*

"If PROF. SEELEY'S volume was remarkable for its originality and the breadth of its views, Mr. ETHERIDGE fully justifies the assertion made in his preface that his book differs in construction and detail from any known manual. . . . Must take HIGH RANK AMONG WORKS OF REFERENCE."—*Athenæum.*

Works by GRENVILLE A. J. COLE, M.R.I.A., F.G.S.,

Professor of Geology in the Royal College of Science for Ireland.

PRACTICAL GEOLOGY
(AIDS IN):

WITH A SECTION ON PALÆONTOLOGY.

By PROFESSOR GRENVILLE COLE, M.R.I.A., F.G.S.

THIRD EDITION, Revised and in part Re-written. With Frontispiece and Illustrations. Cloth, 10s. 6d.

GENERAL CONTENTS.—

PART I.—SAMPLING OF THE EARTH'S CRUST.
PART II.—EXAMINATION OF MINERALS.
PART III.—EXAMINATION OF ROCKS.
PART IV.—EXAMINATION OF FOSSILS.

"Prof. Cole treats of the examination of minerals and rocks in a way that has never been attempted before . . . DESERVING OF THE HIGHEST PRAISE. Here indeed are 'Aids' INNUMERABLE and INVALUABLE. All the directions are given with the utmost clearness and precision."—*Athenæum.*

"To the younger workers in Geology, Prof. Cole's book wil be as INDISPENSABLE as a dictionary to the learners of a language."—*Saturday Review.*

"That the work deserves its title, that it is full of 'AIDS,' and in the highest degree 'PRACTICAL,' will be the verdict of all who use it."—*Nature.*

"This EXCELLENT MANUAL . . . will be A VERY GREAT HELP. . . . The section on the Examination of Fossils is probably the BEST of its kind yet published. . . . FULL of well-digested information from the newest sources and from personal research."—*Annals of Nat. History.*

OPEN-AIR STUDIES:
An Introduction to Geology Out-of-doors.

By PROFESSOR GRENVILLE COLE, M.R.I.A., F.G.S.

With 12 Full-Page Illustrations from Photographs.
Cloth. 8s. 6d.

For details, see p. 86.

Edited by PROFESSOR COLE.

The "New Land" Series for Colonists and Prospectors

(See next page).

LONDON: CHARLES GRIFFIN & CO., LIM.TED, EXETER STREET, STRAND.

ORE & STONE MINING.

BY

C. LE NEVE FOSTER, D.Sc., F.R.S.,

PROFESSOR OF MINING, ROYAL COLLEGE OF SCIENCE H.M. INSPECTOR OF MINES.

SECOND EDITION. With Frontispiece and 716 Illustrations. 34s.

"DR. FOSTER'S book was expected to be EPOCH-MAKING, and it fully justifies such expectation. . . . A MOST ADMIRABLE account of the mode of occurrence of practically ALL KNOWN MINERALS. Probably stands UNRIVALLED for completeness."—*The Mining Journal.*

GENERAL CONTENTS.

INTRODUCTION. Mode of Occurrence of Minerals: Classification: Tabular Deposits, Masses—Examples: Alum, Amber, Antimony, Arsenic, Asbestos, Asphalt, Barytes, Borax, Boric Acid, Carbonic Acid, Clay, Cobalt Ore, Copper Ore, Diamonds, Flint, Freestone, Gold Ore, Graphite, Gypsum, Ice, Iron Ore, Lead Ore, Manganese Ore, Mica, Natural Gas, Nitrate of Soda, Ozokerite, Petroleum, Phosphate of Lime, Potassium Salts, Quicksilver Ore, Salt, Silver Ore, Slate, Sulphur, Tin Ore, Zinc Ore. Faults. **Prospecting:** Chance Discoveries—Adventitious Finds—Geology as a Guide to Minerals—Associated Minerals—Surface Indications. **Boring:** Uses of Bore-holes—Methods of Boring Holes: i. By Rotation, ii. By Percussion with Rods, iii. By Percussion with Rope. **Breaking Ground:** Hand Tools—Machinery—Transmission of Power—Excavating Machinery: i. Steam Diggers, ii. Dredges, iii. Rock Drills, iv. Machines for Cutting Grooves, v. Machines for Tunnelling—Modes of using Holes—Driving and Sinking—Fire-setting—Excavating by Water. **Supporting Excavations:** Timbering—Masonry—Metallic Supports—Watertight Linings—Special Processes. **Exploitation:** Open Works:—Hydraulic Mining—Excavation of Minerals under Water—Extraction of Minerals by Wells and Bore-holes—Underground Workings—Beds—Veins—Masses. **Haulage or Transport:** Underground: by Shoots, Pipes, Persons, Sledges, Vehicles, Railways, Machinery, Boats—Conveyance above Ground. **Hoisting or Winding:** Motors, Drums, and Pulley Frames—Ropes, Chains, and Attachments—Receptacles—Other Appliances—Safety Appliances—Testing Ropes—Pneumatic Hoisting. **Drainage:** Surface Water—Dams—Drainage Tunnels—Siphons—Winding Machinery—Pumping Engines above ground—Pumping Engines below ground—Co-operative Pumping. **Ventilation:** Atmosphere of Mines—Causes of Pollution of Air—Natural Ventilation—Artificial Ventilation: i. Furnace Ventilation, ii. Mechanical Ventilation—Testing the Quality of Air—Measuring the Quantity and Pressure of the Air—Efficiency of Ventilating Appliances—Resistance caused by Friction. **Lighting:** Reflected Daylight—Candles—Torches—Lamps—Wells Light—Safety Lamps—Gas—Electric Light. **Descent and Ascent:** Steps and Slides—Ladders—Buckets and Cages—Man Engine. **Dressing:** i. Mechanical Processes—ii. Processes depending on Physical Properties—iii. Chemical Processes—**Principles of Employment of Mining Labour—Legislation affecting Mines and Quarries. Condition of the Miner—Accidents.**

"This EPOCH-MAKING work . . . appeals to MEN OF EXPERIENCE no less than to students."—*Berg- und Hüttenmännische Zeitung.*

"This SPLENDID WORK."—*Oesterr. Ztschrft. für Berg- und Hüttenwesen.*

ELEMENTARY MINING AND QUARRYING

(An Introductory Text-book).

BY PROF. C. LE NEVE FOSTER, F.R.S.

In Crown 8vo. With Illustrations. [*Shortly.*

COAL-MINING (A Text-Book of):

FOR THE USE OF COLLIERY MANAGERS AND OTHERS ENGAGED IN COAL-MINING.

BY

HERBERT WILLIAM HUGHES, F.G.S.,
Assoc. Royal School of Mines, General Manager of Sandwell Park Colliery.

THIRD EDITION. *In Demy 8vo, Handsome Cloth. With very Numerous Illustrations, mostly reduced from Working Drawings. Price* 18*s.*

"The details of colliery work have been fully described, on the ground that collieries are more often made REMUNERATIVE by PERFECTION IN SMALL MATTERS than by bold strokes of engineering. . . . It frequently happens, in particular localities, that the adoption of a combination of small improvements, any of which viewed separately may be of apparently little value, turns an unprofitable concern into a paying one."—*Extract from Author's Preface.*

GENERAL CONTENTS.

Geology: Rocks—Faults—Order of Succession—Carboniferous System in Britain. **Coal**: Definition and Formation of Coal—Classification and Commercial Value of Coals. **Search for Coal**: Boring—various appliances used—Devices employed to meet Difficulties of deep Boring—Special methods of Boring—Mather & Platt's, American, and Diamond systems—Accidents in Boring—Cost of Boring—Use of Boreholes. **Breaking Ground**: Tools—Transmission of Power: Compressed Air, Electricity—Power Machine Drills—Coal Cutting by Machinery—Cost of Coal Cutting—Explosives—Blasting in Dry and Dusty Mines—Blasting by Electricity—Various methods to supersede Blasting. **Sinking**: Position, Form, and Size of shaft—Operation of getting down to "Stone-head"—Method of proceeding afterwards—Lining shafts—Keeping out Water by Tubbing—Cost of Tubbing—Sinking by Boring—Kind-Chaudron, and Lipmann methods—Sinking through Quicksands—Cost of Sinking. **Preliminary Operations**: Driving underground Roads—Supporting Roof: Timbering, Chocks or Cogs, Iron and Steel Supports and Masonry—Arrangement of Inset. **Methods of Working**: Shaft, Pillar, and Subsidence—Bord and Pillar System—Lancashire Method—Longwall Method—Double Stall Method—Working Steep Seams—Working Thick Seams—Working Seams lying near together—Spontaneous Combustion. **Haulage**: Rails—Tubs—Haulage by Horses—Self-acting Inclines—Direct-acting Haulage—Main and Tail Rope—Endless Chain-Endless Rope—Comparison. **Winding**: Pit Frames—Pulleys—Cages—Ropes—Guides—Engines—Drums—Brakes—Counterbalancing—Expansion—Condensation—Compound Engines—Prevention of Overwinding—Catches at pit top—Changing Tubs—Tub Controllers—Signalling. **Pumping**: Bucket and Plunger Pumps—Supporting Pipes in Shaft—Valves—Suspended lifts for Sinking—Cornish and Bull Engines—Davey Differential Engine—Worthington Pump—Calculations as to size of Pumps—Draining Deep Workings—Dams. **Ventilation**: Quantity of air required—Gases met with in Mines—Coal-dust—Laws of Friction—Production of Air-currents—Natural Ventilation—Furnace Ventilation—Mechanical Ventilators—Efficiency of Fans—Comparison of Furnaces and Fans—Distribution of the Air-current—Measurement of Air-currents. **Lighting**: Naked Lights—Safety Lamps—Modern Lamps—Conclusions—Locking and Cleaning Lamps—Electric Light Underground—Delicate Indicators. **Works at Surface**: Boilers—Mechanical Stoking—Coal Conveyors—Workshops. **Preparation of Coal for Market**: General Considerations—Tipplers—Screens—Varying the Sizes made by Screens—Belts—Revolving Tables—Loading Shoots—Typical Illustrations of the arrangement of Various Screening Establishments—Coal Washing—Dry Coal Cleaning—Briquettes.

"Quite THE BEST BOOK of its kind . . . as PRACTICAL in aim as a book can be . . . touches upon every point connected with the actual working of collieries. The illustrations are EXCELLENT."—*Athenæum.*

"A Text-book on Coal-Mining is a great desideratum, and Mr. HUGHES possesses ADMIRABLE QUALIFICATIONS for supplying it. . . . We cordially recommend the work."—*Colliery Guardian.*

"Mr. HUGHES has had opportunities for study and research which fall to the lot of but few men. If we mistake not, his text-book will soon come to be regarded as the STANDARD WORK of its kind."—*Birmingham Daily Gazette.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

PETROLEUM

AND ITS PRODUCTS:

A PRACTICAL TREATISE.

BY

BOVERTON REDWOOD,
F.R.S.E., F.I.C., Assoc. Inst. C.E.,
Hon. Corr. Mem. of the Imperial Russian Technical Society; Mem. of the American Chemical Society; Consulting Adviser to the Corporation of London under the Petroleum Acts, &c., &c.

Assisted by GEO. T. HOLLOWAY, F.I.C., Assoc. R.C.S.,
And Numerous Contributors.

In Two Volumes, Large 8vo. Price 45s.

With Numerous Maps, Plates, and Illustrations in the Text.

GENERAL CONTENTS.

I. General Historical Account of the Petroleum Industry.
II. Geological and Geographical Distribution of Petroleum and Natural Gas.
III. Chemical and Physical Properties of Petroleum.
IV. Origin of Petroleum and Natural Gas.
V. Production of Petroleum, Natural Gas, and Ozokerite.
VI. The Refining of Petroleum.
VII. The Shale Oil and Allied Industries.
VIII. Transport, Storage, and Distribution of Petroleum.
IX. Testing of Petroleum.
X. Application and Uses of Petroleum.
XI. Legislation on Petroleum at Home and Abroad.
XII. Statistics of the Petroleum Production and the Petroleum Trade, obtained from the most trustworthy and official sources.

"The MOST COMPREHENSIVE AND CONVENIENT ACCOUNT that has yet appeared of a gigantic industry which has made incalculable additions to the comfort of civilised man. . . . The chapter dealing with the arrangement for STORAGE and TRANSPORT of GREAT PRACTICAL INTEREST. . . . The DIGEST of LEGISLATION on the subject cannot but prove of the GREATEST UTILITY."—*The Times.*

"A SPLENDID CONTRIBUTION to our technical literature."—*Chemical News.*

"This THOROUGHLY STANDARD WORK . . . in every way EXCELLENT . . most fully and ably handled . . . could only have been produced by a man in the very exceptional position of the Author. . . . INDISPENSABLE to all who have to do with Petroleum, its APPLICATIONS, MANUFACTURE, STORAGE, or TRANSPORT."—*Mining Journal.*

"We must concede to Mr. Redwood the distinction of having produced a treatise which must be admitted to the rank of THE INDISPENSABLES. It contains THE LAST WORD that can be said about Petroleum in any of its SCIENTIFIC, TECHNICAL, and LEGAL aspects. It would be difficult to conceive of a more comprehensive and explicit account of the geological conditions associated with the SUPPLY of Petroleum and the very practical question of its AMOUNT and DURATION."—*Journal of Gas Lighting.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

MINE-SURVEYING (A Treatise on):

For the use of Managers of Mines and Collieries, Students at the Royal School of Mines, &c.

BY BENNETT H. BROUGH, F.G.S., ASSOC.R.S.M.,

Formerly Instructor of Mine-Surveying, Royal School of Mines.

With Diagrams. SIXTH EDITION, Enlarged and Revised. Cloth, 7s. 6d.

GENERAL CONTENTS.

General Explanations—Measurement of Distances—Miner's Dial—Variation of the Magnetic-Needle—Surveying with the Magnetic-Needle in presence of Iron—Surveying with the Fixed Needle—German Dial—Theodolite—Traversing Underground—Surface-Surveys with Theodolite—Plotting the Survey—Calculation of Areas—Levelling—Connection of Underground- and Surface-Surveys—Measuring Distances by Telescope—Setting-out—Mine-Surveying Problems—Mine Plans—Applications of Magnetic-Needle in Mining—Photographic Surveying—*Appendices.*

"HAS PROVED itself a VALUABLE Text-book; the BEST, if not the only one, in the English language on the subject."—*Mining Journal.*

"No English-speaking Mine Agent or Mining Student will consider his technical library complete without it."—*Nature.*

"A valuable accessory to Surveyors in every department of commercial enterprise. Fully deserves to hold its position as a STANDARD."—*Colliery Guardian.*

In Large 8vo, with Illustrations and Folding-Plates. 10s. 6d.

BLASTING:

AND THE USE OF EXPLOSIVES.

A Handbook for Engineers and others Engaged in Mining, Tunnelling, Quarrying, &c.

BY OSCAR GUTTMANN, ASSOC. M. INST. C.E.

Member of the Societies of Civil Engineers and Architects of Vienna and Budapest, Corresponding Member of the Imp. Roy. Geological Institution of Austria, &c.

GENERAL CONTENTS.—Historical Sketch—Blasting Materials—Blasting Powder—Various Powder-mixtures—Gun-cotton—Nitro-glycerine and Dynamite—Other Nitro-compounds—Sprengel's Liquid (acid) Explosives—Other Means of Blasting—Qualities, Dangers, and Handling of Explosives—Choice of Blasting Materials—Apparatus for Measuring Force—Blasting in Fiery Mines—Means of Igniting Charges—Preparation of Blasts—Bore-holes—Machine-drilling—Chamber Mines—Charging of Bore-holes—Determination of the Charge—Blasting in Bore-holes—Firing—Straw and Fuze Firing—Electrical Firing—Substitutes for Electrical Firing—Results of Working—Various Blasting Operations—Quarrying—Blasting Masonry, Iron and Wooden Structures—Blasting in earth, under water, of ice, &c.

"This ADMIRABLE work."—*Colliery Guardian.*

"Should prove a *vade-mecum* to Mining Engineers and all engaged in practical work. —*Iron and Coal Trades Review.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

NEW VOLUME OF GRIFFIN'S MINING SERIES.

Edited by C. LE NEVE FOSTER, D.Sc., F.R.S.,
H.M. Inspector of Mines, Professor of Mining, Royal School of Mines.

Mine Accounts and Mining Book-keeping,

A Manual for the Use of Students, Managers of Metalliferous Mines and Collieries, Secretaries of Mining Companies, and others interested in Mining.

WITH NUMEROUS EXAMPLES TAKEN FROM THE ACTUAL PRACTICE OF LEADING MINING COMPANIES THROUGHOUT THE WORLD.

BY

JAMES GUNSON LAWN, Assoc. R.S.M., Assoc. Mem. Inst. C.E., F.G.S.,
Professor of Mining at the South African School of Mines, Capetown, Kimberley, and Johannesburg.

In Large 8vo. Price 10s. 6d.

GENERAL CONTENTS.—**Introduction. Part I. Engagement and Payment of Workmen**—Data Determining Gross Amount due to Workmen—A. Length of Time Worked—Overtime—B. Amount of Work done—Sinking and Driving—Exploitation—Sliding Scales—Modifications—C. Value of Mineral gotten—Deductions—Pay-Sheets, Due-Bills, and Pay-Tickets. **Part II. Purchases and Sales**—Purchase and Distribution of Stores—Books and Forms Relating thereto—Sales of Product—Methods of Sale—Contract—Tender—Delivery of, and Payment for, Mineral—Tin Ore—Coal—Silver Ore—Gold Ore **Part III. Working Summaries and Analyses**—Summaries of Minerals Raised, Dressed, and Sold; and of Labour—Analyses of Costs—Accounts Forwarded to Head Office. **Part IV. Ledger, Balance Sheet, and Company Books**—Head Office Books—Ledger—Principal Accounts of a Mining Company—Capital Account—Sale and Purchase Accounts—Capital Expenditure—Personal—Stores—Wages Account—Bad Debts Account—Cash Account—Bills Receivable and Payable Account—Discount and Interest Account—Product Account—Working Accounts—Profit and Loss Account—Journal—Inventory—Balance Sheet—Bibliography—Redemption of Capital—1. Debentures—2. Sinking Fund—A. By Equal Annual Sums—B By Annual Sum varying according to a Formula—C. By Annual Sum depending on Mineral worked—3. Enlarged Dividends or Bonuses—Depreciation—Reserve Fund—Bibliography—General Considerations and Companies Books—Private Individuals—Private Partnership Companies—Cost-book Companies—Limited Liability Companies—Stocks and Shares—Debentures—Books connected with Shares—Miscellaneous Books—Bibliography. **Part V. Reports and Statistics**—Inspections of Workings and Machinery—A. Colliery Reports, &c.—Inspections—Report Books—Measurement of Ventilating Current—Permits to fire Shots and carry Safety Lamp Key—B. Ore Mine Reports, &c—C. Miscellaneous Reports, &c.—Reports of Mining Companies—Managers' Reports—Diagrams—Tabular Statements—Reports of Directors—Reports of Cost-book Mines—Mining Statistics—Great Britain—Other Countries—Bibliography.

"It seems IMPOSSIBLE to suggest how Mr. LAWN'S book could be made more COMPLETE or more VALUABLE, careful, and exhaustive."—*Accountants' Magazine.*

"MR. LAWN'S book should be found of GREAT USE by MINE SECRETARIES and MINE MANAGERS. It consists of five Parts. PART 1 is devoted to the engagement and payment of workmen, and contains forms of contracts and pay sheets of various descriptions in use by Mining Companies in England and South Africa. Special reference is made to pay sheets and forms employed by the DE BEERS CONSOLIDATED MINES, to the General Manager and the late Secretary of which Company the author is indebted for the particulars given. PART 2 is taken up by a description of books and forms relating to the purchases of Stores, &c., and to sales of the Products of the mines. PART 3 is the most important section of the book, containing instructive details of the manner of obtaining summaries of Working Expenditure and Analyses of Costs. The forms used in this connection by the De Beers Company are shown *in extenso*. PART 4 consists of the Bookkeeping, properly so-called, of a mining company. All details concerning the ledger, journal, and other books, and the principal working accounts of a mine are given. There are some very interesting formulæ in this section, showing the manner in which the CAPITAL of a company should be REDEEMED and REPAID to its Shareholders. According to this manual there are three ways in which this extremely desirable end may be arrived at. . . . The book is published at half a guinea, a price low enough considering the amount of information and instruction set forth."—*Johannesburg Star.*

THIRD EDITION. With Folding Plates and Many Illustrations.

Large 8vo. Handsome Cloth. 36s.

ELEMENTS OF METALLURGY:

A PRACTICAL TREATISE ON THE ART OF EXTRACTING METALS FROM THEIR ORES.

BY

J. ARTHUR PHILLIPS, M.INST.C.E., F.C.S., F.G.S., &c.

AND

H. BAUERMAN, V.P.G.S.

GENERAL CONTENTS.

Refractory Materials.	Antimony.	Iron.
Fire-Clays.	Arsenic.	Cobalt.
Fuels, &c.	Zinc.	Nickel.
Aluminium.	Mercury.	Silver.
Copper.	Bismuth.	Gold.
Tin.	Lead.	Platinum.

*** Many NOTABLE ADDITIONS, dealing with new Processes and Developments, will be found in the Third Edition.

"Of the THIRD EDITION, we are still able to say that, as a Text-book of Metallurgy, it is THE BEST with which we are acquainted."—*Engineer.*

"The value of this work is almost *inestimable.* There can be no question that the amount of time and labour bestowed on it is enormous. . . . There is certainly no Metallurgical Treatise in the language calculated to prove of such general utility."—*Mining Journal.*

"In this most useful and handsome volume is condensed a large amount of valuable practical knowledge. A careful study of the first division of the book, on Fuels, will be found to be of great value to every one in training for the practical applications of our scientific knowledge to any of our metallurgical operations."—*Athenæum.*

"A work which is equally valuable to the Student as a Text-book, and to the practical Smelter as a Standard Work of Reference. . . . The Illustrations are admirable examples of Wood Engraving."—*Chemical News.*

Griffin's Metallurgical Series.

STANDARD WORKS OF REFERENCE

FOR

Metallurgists, Mine-Owners, Assayers, Manufacturers, and all interested in the development of the Metallurgical Industries.

EDITED BY

W. C. ROBERTS-AUSTEN, C.B., D.C.L., F.R.S.,

CHEMIST AND ASSAYER TO THE ROYAL MINT; PROFESSOR OF METALLURGY IN THE ROYAL COLLEGE OF SCIENCE.

In Large 8vo, Handsome Cloth. With Illustrations.

1. **INTRODUCTION to the STUDY of METALLURGY.** By the EDITOR. FOURTH EDITION. 15s. (See p. 63.)

2. **GOLD (The Metallurgy of).** By THOS. KIRKE ROSE, D.Sc., Assoc. R.S.M., F.I.C., of the Royal Mint. THIRD EDITION, 21s. (See p. 64.)

3. **IRON (The Metallurgy of).** By THOS. TURNER, Assoc. R.S.M., F.I.C., F.C.S. 16s. (See p. 65.)

Will be Published at Short Intervals.

4. **STEEL (The Metallurgy of).** By F. W. HARBORD, Assoc. R.S.M., F.I.C.

5. **SILVER AND LEAD (The Metallurgy of).** By H. F. COLLINS, Assoc. R.S.M., M.Inst.M.M. *[At Press.*

6. **METALLURGICAL MACHINERY:** the Application of Engineering to Metallurgical Problems. By HENRY CHARLES JENKINS, Wh.Sc., Assoc. R.S.M., Assoc.M.Inst.C.E., of the Royal College of Science.

7. **ALLOYS.** By the EDITOR.

*** Other Volumes in Preparation.

GRIFFIN'S METALLURGICAL SERIES.

FOURTH EDITION, Revised and Enlarged. Price 15s.

AN INTRODUCTION TO THE STUDY

OF

METALLURGY.

BY

W. C. ROBERTS-AUSTEN, C.B., D.C.L., F.R.S.,

Associate of the Royal School of Mines; Chemist and Assayer of the Royal Mint; Professor of Metallurgy in the Royal College of Science.

In Large 8vo, with numerous Illustrations and Micro-Photographic Plates of different varieties of Steel.

GENERAL CONTENTS.

The Relation of Metallurgy to Chemistry.
Physical Properties of Metals.
Alloys.
The Thermal Treatment of Metals.
Fuel and Thermal Measurements.
Materials and Products of Metallurgical Processes
Furnaces.
Means of Supplying Air to Furnaces.
Thermo-Chemistry.
Typical Metallurgical Processes.
The Micro-Structure of Metals and Alloys.
Economic Considerations.

"No English text-book at all approaches this in the COMPLETENESS with which the most modern views on the subject are dealt with. Professor Austen's volume will be INVALUABLE, not only to the student, but also to those whose knowledge of the art is far advanced."—*Chemical News.*

"INVALUABLE to the student. . . . Rich in matter not to be readily found elsewhere."—*Athenæum.*

"This volume amply realises the expectations formed as to the result of the labours of so eminent an authority. It is remarkable for its ORIGINALITY of conception and for the large amount of information which it contains. . . . We recommend every one who desires information not only to consult, but to STUDY this work."—*Engineering.*

"Will at once take FRONT RANK as a text-book."—*Science and Art.*

"Prof. ROBERTS-AUSTEN'S book marks an epoch in the history of the teaching of metallurgy in this country."—*Industries.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

GRIFFIN'S METALLURGICAL SERIES.

THIRD EDITION. Revised and Enlarged. Handsome Cloth. 21s.

THE METALLURGY OF GOLD.

BY

T. KIRKE ROSE, D.Sc.Lond., Assoc.R.S.M.,
Assistant Assayer of the Royal Mint.

Revised and partly Re-written. Including the most recent Improvements in the Cyanide Process. With Frontispiece and numerous Illustrations.

GENERAL CONTENTS.

The Properties of Gold and its Alloys.
Chemistry of the Compounds of Gold.
Mode of Occurrence and Distribution of Gold.
Placer Mining.
Shallow Deposits.
Deep Placer Mining.
Quartz Crushing in the Stamp Battery.
Amalgamation in the Stamp Battery.
Other Forms of Crushing and Amalgamating Machinery.
Concentration in Stamp Mills.
Stamp Battery Practice in particular Localities.
Chlorination: The Preparation of Ore for Treatment.
Chlorination: The Vat Process.
Chlorination: The Barrel Process.
Chlorination: Practice in particular Mills.
The Cyanide Process.
Chemistry of the Cyanide Process.
Pyritic Smelting.
The Refining and Parting of Gold Bullion.
The Assay of Gold Ores.
The Assay of Gold Bullion.
Economic Considerations.
Bibliography.

"A COMPREHENSIVE PRACTICAL TREATISE on this important subject."—*The Times.*

"The MOST COMPLETE description of the CHLORINATION PROCESS which has yet been published."—*Mining Journal.*

"Dr. ROSE gained his experience in the Western States of America, but he has secured details of gold-working from ALL PARTS of the world, and these should be of GREAT SERVICE to practical men. . . . The four chapters on *Chlorination*, written from the point of view alike of the practical man and the chemist, TEEM WITH CONSIDERATIONS HITHERTO UNRECOGNISED, and constitute an addition to the literature of Metallurgy, which will prove to be of classical value."—*Nature.*

"Adapted for all who are interested in the Gold Mining Industry, being free from technicalities as far as possible, but is more particularly of value to those engaged in the industry—viz., mill-managers, reduction-officers, &c."—*Cape Times.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

GRIFFIN'S METALLURGICAL SERIES.

THE METALLURGY OF IRON.

BY

THOMAS TURNER, Assoc.R.S.M., F.I.C.,
Director of Technical Instruction to the Staffordshire County Council.

IN LARGE 8VO, HANDSOME CLOTH, WITH NUMEROUS ILLUSTRATIONS (MANY FROM PHOTOGRAPHS). PRICE 16s.

GENERAL CONTENTS.

Early History of Iron.
Modern History of Iron.
The Age of Steel.
Chief Iron Ores.
Preparation of Iron Ores.
The Blast Furnace.
The Air used in the Blast Furnace.
Reactions of the Blast Furnace.
The Fuel used in the Blast Furnace.
Slags and Fluxes of Iron Smelting.
Properties of Cast Iron.
Foundry Practice.
Wrought Iron.
Indirect Production of Wrought Iron.
The Puddling Process.
Further Treatment of Wrought Iron.
Corrosion of Iron and Steel.

"A MOST VALUABLE SUMMARY of useful knowledge relating to every method and stage in the manufacture of cast and wrought iron down to the present moment . . . particularly rich in chemical details. . . . An EXHAUSTIVE and REALLY NEEDED compilation by a MOST CAPABLE and THOROUGHLY UP-TO-DATE metallurgical authority."—*Bulletin of the American Iron and Steel Association.*

"This is A DELIGHTFUL BOOK, giving, as it does, reliable information on a subject becoming every day more elaborate. . . . The account of the chief iron ores is, like the rest of this work, RICH in detail. . . . Foundry Practice has been made the subject of considerable investigation by the author, and forms an interesting and able chapter."—*Colliery Guardian.*

"Mr. Turner's work comes at an opportune moment and in answer to a REAL DEMAND. . . . A THOROUGHLY USEFUL BOOK, which brings the subject UP TO DATE. The author has produced an EMINENTLY READABLE BOOK. . . . Whatever he describes, he describes well. . . . There is much in the work that will be of GREAT VALUE to those engaged in the iron industry."—*Mining Journal.*

IN PREPARATION.

COMPANION-VOLUME ON

THE METALLURGY OF STEEL.

By F. W. HARBORD, Assoc.R.S.M., F.I.C.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

ASSAYING (A Text-Book of):

For the use of Students, Mine Managers, Assayers, &c.

By J. J. BERINGER, F.I.C., F.C.S.,
Public Analyst for, and Lecturer to the Mining Association of, Cornwall.

And C. BERINGER, F.C.S.,
Late Chief Assayer to the Rio Tinto Copper Company, London.

With numerous Tables and Illustrations. Crown 8vo. Cloth, 10/6.
FOURTH EDITION; Revised.

GENERAL CONTENTS. — PART I. — INTRODUCTORY: MANIPULATION: Sampling; Drying; Calculation of Results—Laboratory-books and Reports. METHODS: Dry Gravimetric; Wet Gravimetric—Volumetric Assays: Titrometric, Colorimetric, Gasometric—Weighing and Measuring—Reagents—Formulæ, Equations, &c.—Specific Gravity.

PART II.—METALS: Detection and Assay of Silver, Gold, Platinum, Mercury, Copper, Lead, Thallium, Bismuth, Antimony, Iron, Nickel, Cobalt, Zinc, Cadmium, Tin, Tungsten, Titanium, Manganese, Chromium, &c.—Earths, Alkalies.

PART III.—NON-METALS: Oxygen and Oxides; The Halogens—Sulphur and Sulphates—Arsenic, Phosphorus, Nitrogen—Silicon, Carbon, Boron—Useful Tables.

"A REALLY MERITORIOUS WORK, that may be safely depended upon either for systematic instruction or for reference."—*Nature.*

"This work is one of the BEST of its kind. . . . Contains all the information that the Assayer will find necessary in the examination of minerals."—*Engineer*

Handsome Cloth. With Numerous Illustrations. 6s.

ELEMENTARY METALLURGY

(A TEXT-BOOK OF).

Including the Author's PRACTICAL LABORATORY COURSE.

By A. HUMBOLDT SEXTON, F.I.C., F.C.S.,
Professor of Metallurgy in the Glasgow and West of Scotland Technical College.

GENERAL CONTENTS.—Introduction—Properties of the Metals—Combustion—Fuels—Refractory Materials—Furnaces—Occurrence of the Metals in Nature—Preparation of the Ore for the Smelter—Metallurgical Processes—Iron: Preparation of Pig Iron—Malleable Iron—Steel—Mild Steel—Copper—Lead—Zinc and Tin—Silver—Gold—Mercury—Alloys—Applications of ELECTRICITY to Metallurgy—LABORATORY COURSE WITH NUMEROUS PRACTICAL EXERCISES.

'Just the kind of work for Students COMMENCING the study of Metallurgy, or for ENGINEERING Students requiring a GENERAL KNOWLEDGE of it, or for ENGINEERS in practice who like a HANDY WORK of REFERENCE. To all three classes we HEARTILY commend the work."—*Practical Engineer.*

"EXCELLENTLY got-up and WELL-ARRANGED. . . . Iron and copper well explained by EXCELLENT diagrams showing the stages of the process from start to finish. . . . The most NOVEL chapter is that on the many changes wrought in Metallurgical Methods by ELECTRICITY."—*Chemical Trade Journal.*

"Possesses the GREAT ADVANTAGE of giving a COURSE OF PRACTICAL WORK."—*Mining Journal.*

In large 8vo. With Numerous Illustrations and Three Folding-Plates.
Price 21s.

ELECTRIC SMELTING & REFINING:

A PRACTICAL MANUAL OF

THE EXTRACTION AND TREATMENT OF METALS BY ELECTRICAL METHODS.

Being the "ELEKTRO-METALLURGIE" of

DR. W. BORCHERS.

Translated from the Second German Edition

BY WALTER G. McMILLAN, F.I.C., F.C.S.,

Secretary to the Institution of Electrical Engineers; late Lecturer in Metallurgy at Mason College, Birmingham.

*** THE PUBLISHERS beg to call attention to this valuable work. Dr. BORCHERS' treatise is PRACTICAL throughout. It confines itself to ONE branch of Electro-Chemistry, viz.:—ELECTROLYSIS, a subject which is daily becoming of more and more importance to the Practical Metallurgist and Manufacturer. Already in the extraction of Aluminium, the refining of Copper, the treatment of Gold and other metals, electrical processes are fast taking the place of the older methods. Dr. BORCHERS' work is acknowledged as the standard authority on the subject in Germany.

CONTENTS.

PART I.—ALKALIES AND ALKALINE EARTH METALS: Magnesium, Lithium, Beryllium, Sodium, Potassium, Calcium, Strontium, Barium, the Carbides of the Alkaline Earth Metals.

PART II.—THE EARTH METALS: Aluminium, Cerium, Lanthanum, Didymium.

PART III.—THE HEAVY METALS: Copper, Silver, Gold, Zinc and Cadmium, Mercury, Tin, Lead, Bismuth, Antimony, Chromium, Molybdenum, Tungsten, Uranium, Manganese, Iron, Nickel, and Cobalt, the Platinum Group.

"COMPREHENSIVE and AUTHORITATIVE . . . not only FULL of VALUABLE INFORMATION, but gives evidence of a THOROUGH INSIGHT into the technical VALUE and POSSIBILITIES of all the methods discussed."—*The Electrician.*

"Dr. BORCHERS' WELL-KNOWN WORK . . . must OF NECESSITY BE ACQUIRED by every one interested in the subject. EXCELLENTLY put into English with additional matter by Mr. M'MILLAN . . . the PHENOMENAL RAPIDITY with which the practical applications of ELECTRO-METALLURGY are advancing in Germany and in America, affords much material for reflection to Engineers in England."—*Nature.*

"Will be of GREAT SERVICE to the practical man and the Student."—*Electric Smelting.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SECOND EDITION in Preparation.

ELECTRO-METALLURGY

(A TREATISE ON):

Embracing the Application of Electrolysis to the Plating, Depositing, Smelting, and Refining of various Metals, and to the Reproduction of Printing Surfaces and Art-Work, &c.

BY

WALTER G. McMILLAN, F.I.C., F.C.S.

With numerous Illustrations. Large Crown 8vo. Cloth.

"This excellent treatise, . . . one of the BEST and MOST COMPLETE manuals hitherto published on Electro-Metallurgy."—*Electrical Review.*

"This work will be a STANDARD."—*Jeweller.*

"Any metallurgical process which REDUCES the COST of production must of necessity prove of great commercial importance. . . . We recommend this manual to ALL who are interested in the PRACTICAL APPLICATION of electrolytic processes."—*Nature.*

The Art of the Goldsmith and Jeweller

(A Manual for Students and Practical Men).

BY THOS. B. WIGLEY,

Headmaster of the Jewellers and Silversmiths' Association Technical School, Birmingham.

ASSISTED BY

J. H. STANSBIE, B.Sc. (LOND.), F.I.C.,

Lecturer at the Birmingham Municipal Technical School.

In Large Crown 8vo. With Numerous Illustrations.

§ 9. Griffin's Chemical and Technological Publications.

		PAGE
Inorganic Chemistry,	Profs. Dupré and Hake,	70
Quantitative Analysis,	Prof. Humboldt Sexton,	70
Qualitative ,,	,, ,,	70
Chemical Experiments,	Dr. Alder Wright,	80
,, Recreations,	J. J. Griffin,	75
Chemistry for Engineers,	MM. Blount and Bloxam,	71
,, ,, Manufacturers,	,, ,,	71
Tables for Chemists and Manufacturers,	Prof. Castell-Evans,	75
Metallurgy and Electro-Metallurgy,	*See Previous Section.*	
Agricultural Chemistry,	Prof. J. M. Munro,	75
Dairy ,,	H. D. Richmond,	75
Foods, Analysis of,	A. Wynter Blyth,	72
Poisons, Detection of,	,,	72
Technical Mycology (The Fermentation Industries)	Lafar and Salter,	79
Brewing,	Dr. W. J. Sykes,	78
Cements,	G. R. Redgrave,	76
Gas Manufacture,	W. Atkinson Butterfield,	74
Petroleum,	MM. Redwood and Holloway,	58
Oils, Soaps, Candles,	Dr. Alder Wright,	80
Painters' Colours, Oils, and Varnishes,	G. H. Hurst,	76
Painting and Decorating,	W. J. Pearce,	77
Colour Theory	G. H. Hurst,	76
Pharmacy,	Wm. Elborne,	75
Photography,	A. Brothers,	73
The Textile Industries:		
Dyeing,	MM. Knecht and Rawson,	81
,, and Cleaning,	G. H. Hurst,	83
Bleaching and Calico-Printing,	Geo. Duerr,	83
Textile Printing,	Seymour Rothwell,	82

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

INORGANIC CHEMISTRY

(A SHORT MANUAL OF).

BY

A. DUPRÉ, Ph.D., F.R.S.,

AND

WILSON HAKE, Ph.D., F.I.C., F.C.S.,

Of the Westminster Hospital Medical School.

SECOND EDITION, Revised. Crown 8vo. Cloth, 7s. 6d.

"A well-written, clear and accurate Elementary Manual of Inorganic Chemistry. . . . We agree heartily in the system adopted by Drs. Dupré and Hake. WILL MAKE EXPERIMENTAL WORK TREBLY INTERESTING BECAUSE INTELLIGIBLE."—*Saturday Review.*

"There is no question that, given the PERFECT GROUNDING of the Student in his Science, the remainder comes afterwards to him in a manner much more simple and easily acquired The work IS AN EXAMPLE OF THE ADVANTAGES OF THE SYSTEMATIC TREATMENT of a Science over the fragmentary style so generally followed. BY A LONG WAY THE BEST of the small Manuals for Students."—*Analyst.*

LABORATORY HANDBOOKS BY A. HUMBOLDT SEXTON,

Professor of Metallurgy in the Glasgow and West of Scotland Technical College.

Sexton's (Prof.) Outlines of Quantitative Analysis.

FOR THE USE OF STUDENTS.

With Illustrations. FOURTH EDITION. Crown 8vo, Cloth, 3s.

"A COMPACT LABORATORY GUIDE for beginners was wanted, and the want has been WELL SUPPLIED. . . . A good and useful book."—*Lancet.*

Sexton's (Prof.) Outlines of Qualitative Analysis.

FOR THE USE OF STUDENTS.

With Illustrations. THIRD EDITION. Crown 8vo, Cloth, 3s. 6d.

"The work of a thoroughly practical chemist."—*British Medical Journal.*
"Compiled with great care, and will supply a want."—*Journal of Education.*

Sexton's (Prof.) Elementary Metallurgy:

Including the Author's Practical Laboratory Course. With many Illustrations, 6s. [See p. 66.

"Just the kind of work for students commencing the study of metallurgy."—*Practical Engineer.*

CHEMISTRY FOR ENGINEERS AND MANUFACTURERS.

A PRACTICAL TEXT-BOOK.

BY

BERTRAM BLOUNT, AND A. G. BLOXAM,

F.I.C., F.C.S., Assoc. Inst. C.E., Consulting Chemist to the Crown Agents for the Colonies.

F.I.C., F.C.S., Consulting Chemist, Head of the Chemistry Department, Goldsmiths' Inst., New Cross.

With Illustrations. In Two Vols., Large 8vo. Sold Separately.

"The authors have SUCCEEDED beyond all expectations, and have produced a work which should give FRESH POWER to the Engineer and Manufacturer."—*The Times.*

VOLUME I. Price 10s. 6d.

CHEMISTRY OF ENGINEERING, BUILDING, AND METALLURGY.

General Contents.—**INTRODUCTION—Chemistry of the Chief Materials of Construction—Sources of Energy—Chemistry of Steam-raising—Chemistry of Lubrication and Lubricants—Metallurgical Processes used in the Winning and Manufacture of Metals.**

"PRACTICAL THROUGHOUT . . . an ADMIRABLE TEXT-BOOK, useful not only to Students, but to ENGINEERS and MANAGERS OF WORKS in PREVENTING WASTE and IMPROVING PROCESSES."—*Scotsman.*

"EMINENTLY PRACTICAL."—*Glasgow Herald.*

"A book worthy of HIGH RANK . . . its merit is great . . . treatment of the subject of GASEOUS FUEL particularly good. . . . WATER GAS and the production clearly worked out. . . . Altogether a most creditable production. WE WARMLY RECOMMEND IT, and look forward with keen interest to the appearance of Vol. II."—*Journal of Gas Lighting.*

VOLUME II. Price 16s.

THE CHEMISTRY OF MANUFACTURING PROCESSES.

General Contents.—**Sulphuric Acid Manufacture—Manufacture of Alkali, &c.—Destructive Distillation—Artificial Manure Manufacture—Petroleum—Lime and Cement—Clay Industries and Glass—Sugar and Starch—Brewing and Distilling—Oils, Resins, and Varnishes—Soap and Candles—Textiles and Bleaching — Colouring Matters, Dyeing, and Printing — Paper and Pasteboard—Pigments and Paints—Leather, Glue, and Size—Explosives and Matches—Minor Chemical Manufactures.**

"Certainly a GOOD and USEFUL BOOK, constituting a PRACTICAL GUIDE for students by affording a clear conception of the numerous processes as a whole."—*Chemical Trade Journal.*

"We CONFIDENTLY RECOMMEND this volume as a PRACTICAL, and not overloaded, TEXT-BOOK, of GREAT VALUE to students."—*The Builder.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

WORKS BY A. WYNTER BLYTH, M.R.C.S., F.C.S.,

Barrister-at-Law, Public Analyst for the County of Devon, and Medical Officer of Health for St. Marylebone.

FOODS:

THEIR COMPOSITION AND ANALYSIS.

In Demy 8vo, with Elaborate Tables, Diagrams, and Plates. Handsome Cloth. FOURTH EDITION. Price 21s.

GENERAL CONTENTS.

History of Adulteration—Legislation, Past and Present—Apparatus useful to the Food-Analyst—"Ash"—Sugar—Confectionery—Honey—Treacle—Jams and Preserved Fruits—Starches—Wheaten-Flour—Bread—Oats—Barley—Rye—Rice—Maize—Millet—Potato—Peas—Chinese Peas—Lentils—Beans—MILK—Cream—Butter—Oleo-Margarine—Butterine—Cheese—Lard—Tea—Coffee—Cocoa and Chocolate—Alcohol—Brandy—Rum—Whisky—Gin—Arrack—Liqueurs—Absinthe—Principles of Fermentation—Yeast—Beer—Wine—Vinegar—Lemon and Lime Juice—Mustard—Pepper—Sweet and Bitter Almond—Annatto—Olive Oil—WATER—Standard Solutions and Reagents. *Appendix:* Text of English and American Adulteration Acts.

PRESS NOTICES OF THE FOURTH EDITION.

"Simply INDISPENSABLE in the Analyst's laboratory."—*The Lancet.*

"THE STANDARD WORK on the subject. . . . Every chapter and every page gives abundant proof of the strict revision to which the work has been subjected. . . . The section on MILK is, we believe, the most exhaustive study of the subject extant. . . . AN INDISPENSABLE MANUAL for Analysts and Medical Officers of Health."—*Public Health.*

"A new edition of Mr. Wynter Blyth's Standard work, ENRICHED WITH ALL THE RECENT DISCOVERIES AND IMPROVEMENTS, will be accepted as a boon."—*Chemical News.*

POISONS:

THEIR EFFECTS AND DETECTION.

THIRD EDITION. In Large 8vo, Cloth, with Tables and Illustrations. Price 21s.

GENERAL CONTENTS.

I.—Historical Introduction. II.—Classification—Statistics—Connection between Toxic Action and Chemical Composition—Life Tests—General Method of Procedure—The Spectroscope—Examination of Blood and Blood Stains. III.—Poisonous Gases. IV.—Acids and Alkalies. V.—More or less Volatile Poisonous Substances. VI.—Alkaloids and Poisonous Vegetable Principles. VII.—Poisons derived from Living or Dead Animal Substances. VIII.—The Oxalic Acid Group. IX.—Inorganic Poisons. *Appendix:* Treatment, by Antidotes or otherwise, of Cases of Poisoning.

"Undoubtedly THE MOST COMPLETE WORK on Toxicology in our language."—*The Analyst (on the Third Edition).*

"AS A PRACTICAL GUIDE, we know NO BETTER work."—*The Lancet (on the Third Edition).*

*** In the THIRD EDITION, Enlarged and partly Re-written, NEW ANALYTICAL METHODS have been introduced, and the CADAVERIC ALKALOIDS, or PTOMAINES, bodies playing so great a part in Food-poisoning and in the Manifestations of Disease, have received special attention.

SECOND EDITION, in Active Preparation.

PHOTOGRAPHY:

ITS HISTORY, PROCESSES, APPARATUS, AND MATERIALS.

A PRACTICAL MANUAL.

Comprising Working Details of all the More Important Methods.

BY

A. BROTHERS, F.R.A.S.

WITH NUMEROUS FULL PAGE PLATES BY MANY OF THE PROCESSES DESCRIBED, AND ILLUSTRATIONS IN THE TEXT.

In Large 8vo, Handsome Cloth.

GENERAL CONTENTS.

PART. I.—INTRODUCTORY: Historical Sketch; Chemistry and Optics of Photography; Artificial Light.

PART II.—Photographic Processes.

PART III.—Apparatus.

PART IV.—Materials.

PART V.—Applications of Photography; Practical Hints.

"Mr. Brothers has had an experience in Photography so large and varied that any work by him cannot fail to be interesting and valuable. . . . A MOST COMPREHENSIVE volume, entering with full details into the various processes, and VERY FULLY illustrated. The PRACTICAL HINTS are of GREAT VALUE. . . . Admirably got up."—*Brit. Jour. of Photography.*

"For the illustrations alone, the book is most interesting; but, apart from these, the volume is valuable, brightly and pleasantly written, and MOST ADMIRABLY ARRANGED."—*Photographic News.*

"Certainly the FINEST ILLUSTRATED HANDBOOK to Photography which has ever been published. Should be on the reference shelves of every Photographic Society."—*Amateur Photographer.*

"A handbook so far in advance of most others, that the Photographer must not fail to obtain a copy as a reference work."—*Photographic Work.*

"The COMPLETEST HANDBOOK of the art which has yet been published."—*Scotsman.*

*** The New Edition will include all the NEWER DEVELOPMENTS in Photographic Methods, together with Special Articles on RADIOGRAPHY (the X Rays), COLOUR PHOTOGRAPHY, and many New Plates.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

SECOND EDITION, Revised and Enlarged, with NEW SECTION on ACETYLENE.

GAS MANUFACTURE

(THE CHEMISTRY OF).

A Hand-Book on the Production, Purification, and Testing of Illuminating Gas, and the Assay of the Bye-Products of Gas Manufacture. For the Use of Students.

BY

W. J. ATKINSON BUTTERFIELD, M.A., F.I.C., F.C.S.,
Formerly Head Chemist, Gas Works, Beckton, London, E.

With Numerous Illustrations. *Handsome Cloth.*

"The BEST WORK of its kind which we have ever had the pleasure of reviewing."—*Journal of Gas Lighting.*

"Amongst works not written in German, WE RECOMMEND BEFORE ALL OTHERS, BUTTERFIELD'S CHEMISTRY OF GAS MANUFACTURE."—*Chemiker Zeitung.*

GENERAL CONTENTS.

I. Raw Materials for Gas Manufacture.
II. Coal Gas.
III. Carburetted Water Gas.
IV. Oil Gas.
V. Enriching by Light Oils.
VI. Final Details of Manufacture.
VII. Gas Analysis.
VIII. Photometry.
IX. Applications of Gas.
X. Bye-Products.
XI. Acetylene.

*** This work deals primarily with the ordinary processes of GAS MANUFACTURE employed in this country, and aims especially at indicating the *principles* on which they are based. The more modern, but as yet subsidiary, processes are fully treated also.

The Chapters on **Gas Analysis** and **Photometry** will enable the consumer to grasp the methods by which the quality of the gas he uses is ascertained, and in the Chapter on **The Applications of Gas**, not only is it discussed as an illuminant, but also as a ready source of heat and power.

The **Incandescent Gas Light** is dealt with in an exhaustive manner, and the latest theories of its physical basis, as well as the practical developments of lighting by **Incandescence**, are thoroughly discussed.

In Chapter X. an attempt has been made to trace in a readily-intelligible manner the extraction of the principal derivatives from the crude BYE-PRODUCTS.

The work deals incidentally with the most modern features of the industry, including *inter alia* the commercial production and uses of **Acetylene**, to which a special Chapter is devoted in the new Edition, and the application of **compressed gas** for Street Traction. The needs of the Students in Technical Colleges and Classes have throughout been kept in view.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

CASTELL-EVANS (Prof. J., F.I.C., F.C.S., Finsbury Technical College):

TABLES AND DATA for the use of ANALYSTS, CHEMICAL MANUFACTURERS, and SCIENTIFIC CHEMISTS. In Large 8vo. Strongly Bound. [*Shortly.*

*** This important Work will comprehend as far as possible ALL RULES AND TABLES required by the Analyst, Brewer, Distiller, Acid- and Alkali-Manufacturer, &c., &c.; and also the principal data in THERMO-CHEMISTRY, ELECTRO-CHEMISTRY, and the various branches of CHEMICAL PHYSICS which are constantly required by the Student and Worker in Original Research.

Every possible care has been taken to ensure perfect accuracy, and to include the results of the most recent investigations.

ELBORNE (Wm., B.A., F.L.S., F.C.S.):

PRACTICAL PHARMACY. (See p. 106 *General Catalogue*).

GRIFFIN (John Joseph, F.C.S.):

CHEMICAL RECREATIONS: A Popular Manual of Experimental Chemistry. With 540 Engravings of Apparatus. *Tenth Edition.* Crown 8vo. Cloth. Complete in one volume, Parts I. and II. Cloth, gilt top, 12/6.

Part II.—The Chemistry of the Non-Metallic Elements, 10/6.

MUNRO (J. M. H., D.Sc., Professor of Chemistry, Downton College of Agriculture):

AGRICULTURAL CHEMISTRY AND ANALYSIS: A PRACTICAL HAND-BOOK for the Use of Agricultural Students. (*Griffin's Technological Manuals.*)

RICHMOND (H. Droop, F.C.S., Chemist to the Aylesbury Dairy Company):

DAIRY CHEMISTRY FOR DAIRY MANAGERS, CHEMISTS, and ANALYSTS: A Practical Handbook. (*Griffin's Technological Manuals.*)

Painters' Colours, Oils, & Varnishes:

A PRACTICAL MANUAL.

By GEORGE H. HURST, F.C.S.,

Member of the Society of Chemical Industry; Lecturer on the Technology of Painters' Colours, Oils, and Varnishes, the Municipal Technical School, Manchester.

SECOND EDITION, Revised and Enlarged. With Illustrations. 12s. 6d.

GENERAL CONTENTS.—Introductory—THE COMPOSITION, MANUFACTURE, ASSAY, and ANALYSIS of PIGMENTS, White, Red, Yellow and Orange, Green, Blue, Brown, and Black—LAKES—Colour and Paint Machinery—Paint Vehicles (Oils, Turpentine, &c., &c.)—Driers—VARNISHES.

"This useful book will prove MOST VALUABLE."—*Chemical News.*

"A *practical* manual in every respect . . . EXCEEDINGLY INSTRUCTIVE. The section on Varnishes the most reasonable we have met with."—*Chemist and Druggist.*

"VERY VALUABLE information is given."—*Plumber and Decorator.*

"A THOROUGHLY PRACTICAL book, . . . the ONLY English work that satisfactorily treats of the manufacture of oils, colours, and pigments."—*Chemical Trades' Journal.*

"Throughout the work are scattered hints which are INVALUABLE."—*Invention.*

*** For Mr. HURST'S GARMENT DYEING AND CLEANING, see p. 83.

In Crown 8vo, Extra. With Illustrations. 8s. 6d.

CALCAREOUS CEMENTS:

THEIR NATURE, PREPARATION, AND USES.

With some Remarks upon Cement Testing.

BY

GILBERT R. REDGRAVE, ASSOC. INST. C.E.

GENERAL CONTENTS.—Introduction—Historical Review of the Cement Industry—The Early Days of Portland Cement—Composition of Portland Cement—PROCESSES OF MANUFACTURE—The Washmill and the Backs—Flue and Chamber Drying Processes—Calcination of the Cement Mixture—Grinding of the Cement—Composition of Mortar and Concrete—CEMENT TESTING — CHEMICAL ANALYSIS of Portland Cement, Lime, and Raw Materials — Employment of Slags for Cement Making — Scott's Cement, Selenitic Cement, and Cements produced from Sewage Sludge and the Refuse from Alkali Works — Plaster Cements — Specifications for Portland Cement—Appendices (Gases Evolved from Cement Works, Effects of Sea-water on Cement, Cost of Cement Manufacture, &c., &c.)

"A work calculated to be of GREAT and EXTENDED UTILITY."—*Chemical News.*

"INVALUABLE to the Student, Architect, and Engineer."—*Building News.*

"A work of the GREATEST INTEREST and USEFULNESS, which appears at a very critical period of the Cement Trade."—*Brit. Trade Journal.*

"Will be useful to ALL interested in the MANUFACTURE, USE, and TESTING of Cements."—*Engineer.*

Painting and Decorating:

A Complete Practical Manual for House Painters and Decorators.

Embracing the Use of Materials, Tools, and Appliances; the Practical Processes involved; and the General Principles of Decoration, Colour, and Ornament.

BY

WALTER JOHN PEARCE,

LECTURER AT THE MANCHESTER TECHNICAL SCHOOL FOR HOUSE-PAINTING AND DECORATING.

In Crown 8vo. extra. With Numerous Illustrations and Plates (some in Colours), including Original Designs. 12s. 6d.

GENERAL CONTENTS.

Introduction—Workshop and Stores—Plant and Appliances—Brushes and Tools—Materials: Pigments, Driers, Painters' Oils—Wall Hangings—Paper Hanging—Colour Mixing—Distempering—Plain Painting—Staining—Varnish and Varnishing—Imitative Painting—Graining—Marbling—Gilding—Sign-Writing and Lettering—Decoration: General Principles—Decoration in Distemper—Painted Decoration—Relievo Decoration—Colour—Measuring and Estimating—Coach-Painting—Ship-Painting.

"A THOROUGHLY USEFUL BOOK . . . gives GOOD, SOUND, PRACTICAL INFORMATION in a CLEAR and CONCISE FORM. . . . Can be confidently recommended alike to Student and Workman, as well as to those carrying on business as House-Painters and Decorators."—*Plumber and Decorator.*

"A THOROUGHLY GOOD AND RELIABLE TEXT-BOOK. . . . SO FULL and COMPLETE that it would be difficult to imagine how anything further could be added about the Painter's craft."—*Builders' Journal.*

*** MR. PEARCE'S work is the outcome of many years' practical experience, and will be found invaluable by all interested in the subjects of which it treats. It forms the Companion-Volume to MR. GEO. HURST'S well-known work on "PAINTERS' COLOURS" (see p. 76).

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

In Large 8vo. Handsome Cloth. Price 21s.

BREWING:

THE PRINCIPLES AND PRACTICE OF.

FOR THE USE OF STUDENTS AND PRACTICAL MEN.

BY

WALTER J. SYKES, M.D., D.P.H., F.I.C.,
EDITOR OF "THE ANALYST."

With Plate and Illustrations.

"A volume of Brewing Science, which has long been awaited. . . . We consider it one of THE MOST COMPLETE in CONTENTS and NOVEL IN ARRANGEMENT that has yet been published. . . . Will command a large sale."—*The Brewers' Journal.*

"The appearance of a work such as this serves to remind us of the ENORMOUSLY RAPID ADVANCES made in our knowledge of the Scientific Principles underlying the Brewing Processes. . . . Dr. Sykes' work will undoubtedly be of the GREATEST ASSISTANCE, not merely to Brewers, but to all Chemists and Biologists interested in the problems which the Fermentation industries present."—*The Analyst.*

"The publication of DR. SYKES' MASTERLY TREATISE on the art of Brewing is quite an event in the Brewing World. . . . Deserves our warmest praise. . . . A better guide than Dr. Sykes could hardly be found."—*County Brewers' Gazette.*

GENERAL CONTENTS.

I. **Physical Principles involved in Brewing Operations:** Heat: The Thermometer—Specific Heat—Latent Heat—Evaporation—Density and Specific Gravity—Hydrometers. **Chemistry, with special reference to the materials used in Brewing.**

II. **The Microscope:** General Description of the—Microscopical Manipulation—Examination of Yeast—Hanging-Drop Method—Examination of Bacteria—Microscopical Preparations—Bacteriological Methods—Bacteriological Examination of Water—Hansen's Method—Wichmann's Method—Bacteriological Examination of Air. **Vegetable Biology:** The Living Cell—Osmosis—The Yeasts—The Mycoderms—The Torulæ, &c.—The Bacteria—Fermentation and Putrefaction—Bacterium termo—Butyric Acid Bacteria, &c—The Mould Fungi—Mucor mucedo, &c.—Simple Multicellular Organisms—Penicillium glaucum, &c.—Mould Fungi Dangerous on Brewing Premises—The Higher Plants—Germination of Barley—Structure of Barleycorn. **Fermentation:** Ancient—Views of Liebig on—The Physiological Theory—Doctrine of Spontaneous Evolution—Sterilisation of Organic Fluids—Competition amongst Micro-Organisms—Distribution of Atmospheric Germs—Hansen's Investigations on the Air of Breweries—Pasteur's Experiments and Theory—Other Theories of Fermentation—Investigations of Hansen—Pure Cultures from a Single Cell—Introduction of Pure Yeast Cultures into the Brewery—Hansen's and other Pure Yeast Cultivation Apparatus—Advantages of Hansen's Pure Single-Cell Yeast—Differences in the Action of the various Yeasts

III. **Water:** Occurrence and Composition of—Results of Analysis of—Hardness—Waters Suitable for the Production of Different Classes of Ale—Artificial Treatment of Waters—Kainit—Influence of Boiling—Organic Constitution—Effect of Filtration—Methods of Water Analysis—Microscopic Examination of Water Sediments. **Barley and Malting:** Barley—Choice of—Vitality—Age—Malting—Steepings—Steep-Water—Germination of Barley—Flooring—Sprinkling—Withering—Pneumatic Malting—Galland's System—Saladin's—Hemming's—Drying Kiln—Changes Effected in Drying—Storage—Chemical Examination of Barley—Malt Substitutes—Quality of Malt—Chemical Examination of Malt—Ready-formed Sugars—Maltol. **Brewery Plant:** Gravitation Brewery—Cold and Hot Liquor Backs—Malt Mill—Mash Tun, &c.—Coppers—Coolers—Refrigerators—Collecting and Fermenting Vessels—Burton Union System—Attemperators—Parachutes—Racking Squares—Vats and Casks. **Brewing:** Estimation of Quantities for the Brew—Amount of Liquor Required—Hardening Materials—Mashing—Use of Subsidiary Apparatus—Black Beers—Sparging—Boiling—Action of Hop-tannin Bodies—Cooling—Refrigerating—Collection of Wort—Extract Yielded—Fermentation—Addition of Yeast—Change of Yeast—Fermentation Temperatures—Dressing—Appearance of Heads—Cleansing System—Stone Square System—Settling and Racking—Dry Hopping—Secondary Fermentation—Priming—Antiseptics—Fining—Bottled Ales and Bottling. **Beer and its Diseases:** Flavour and Aroma—Condition—Palate Fulness—Head—Brightness—Turbidity—Ropiness—Bibliography—**Appendices:** Solution Weight and Solution Factor—Specific Rotatory Power—The Law of Definite Relation—Alcoholic Fermentation without Yeast-Cells—Fermentation in a Vacuum—**Index.**

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

Vol. I. now Ready. Complete in Itself. Price 15s.

In Large 8vo. Handsome Cloth. With numerous Illustrations.

TECHNICAL MYCOLOGY:

THE UTILIZATION OF MICRO-ORGANISMS IN THE ARTS AND MANUFACTURES.

A Practical Handbook on Fermentation and Fermentative Processes for the Use of Brewers and Distillers, Analysts, Technical and Agricultural Chemists, and all interested in the Industries dependent on Fermentation.

BY DR. FRANZ LAFAR,

Professor of Fermentation-Physiology and Bacteriology in the Technical High School, Vienna.

With an Introduction by DR. EMIL CHR. HANSEN, Principal of the Carlsberg Laboratory, Copenhagen.

TRANSLATED BY CHARLES T. C. SALTER.

In Two Volumes, sold Separately.

"AN EXCEEDINGLY USEFUL WORK, which deals in a thoroughly scientific spirit with TECHNICAL BACTERIOLOGY."—*Nature.*

"We MOST CORDIALLY recommend Dr. Lafar's work to the members of our profession. . . . Must have cost its author an ENORMOUS AMOUNT OF LABOUR AND RESEARCH. No one will fail to observe how well Mr. Salter has done his part."—*The Brewers' Journal.*

"The chapters TERM with INTERESTING MATTER from beginning to end. . . . The plan is ADMIRABLE, the classification simple, the style good, and the tendency of the whole work to convey SURE INFORMATION to the reader."—*The Lancet.*

"Should prove of the UTMOST VALUE to Pharmacists, Chemists, Agriculturists, and many others directly or indirectly concerned in the utilisation of Micro-organisms in the Arts and Manufactures. It is difficult to conceive of a more satisfactory practical handbook."—*Pharmaceutical Journal.*

*** The extraordinary *rôles* played by Micro-organisms in Brewing and Distilling—in the manufacture of Sugar, of Vinegar, and Acetic Acid—in Tanning and Tobacco Manufacture—in Agricultural Industries and the Processes connected with the Dairy: Souring of Cream, Cheese-Ripening, &c., &c.—combine to make Dr. Lafar's Text-Book one of great value and interest to a very wide circle of readers. It is hoped that both Volumes of the English version will be issued during 1898.

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

WORKS BY DR. ALDER WRIGHT, F.R.S.

Fixed Oils, Fats, Butters, and Waxes:

THEIR PREPARATION AND PROPERTIES,

AND THE

MANUFACTURE THEREFROM OF CANDLES, SOAPS, AND OTHER PRODUCTS.

BY

C. R. ALDER WRIGHT, D.Sc., F.R.S.,

Late Lecturer on Chemistry, St. Mary's Hospital Medical School; Examiner in "Soap" to the City and Guilds of London Institute.

In Large 8vo. Handsome Cloth. With 144 Illustrations. 28s.

"Dr. WRIGHT'S work will be found ABSOLUTELY INDISPENSABLE by every Chemist. TERMS with information valuable alike to the Analyst and the Technical Chemist."—*The Analyst.*

"Will rank as the STANDARD ENGLISH AUTHORITY on OILS and FATS for many years to come."—*Industries and Iron.*

*** For other Works on OILS, consult REDWOOD on PETROLEUM (p. 58), and HURST on PAINTERS' COLOURS, OILS, and VARNISHES (p. 76).

SECOND EDITION. With very Numerous Illustrations. Handsome Cloth, 6s.
Also Presentation Edition, Gilt and Gilt Edges, 7s. 6d.

THE THRESHOLD OF SCIENCE:

Simple and Amusing Experiments (over 400) in Chemistry and Physics.

BY C. R. ALDER WRIGHT, D. Sc., F. R. S.,

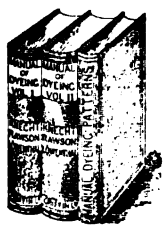
Late Lecturer on Chemistry, St. Mary's Hospital Medical School.

"Any one who may still have doubts regarding the value of Elementary Science as an organ of education will speedily have his doubts dispelled, if he takes the trouble to understand the methods recommended by Dr. Alder Wright."—*Nature.*

"Step by step the learner is here gently guided through the paths of Science, made easy by the perfect knowledge of the teacher, and made flowery by the most striking and curious experiments. Well adapted to become the TREASURED FRIEND of many a bright and promising lad."—*Manchester Examiner.*

§10. THE TEXTILE INDUSTRIES.

"The MOST VALUABLE and USEFUL WORK on Dyeing that has yet appeared in the English language . . . likely to be THE STANDARD WORK OF REFERENCE for years to come."—*Textile Mercury.*



In Two Large 8vo Volumes, 920 pp., with a SUPPLEMENTARY Volume, containing Specimens of Dyed Fabrics. 45s.

A

MANUAL OF DYEING:

FOR THE USE OF PRACTICAL DYERS, MANUFACTURERS, STUDENTS, AND ALL INTERESTED IN THE ART OF DYEING.

BY

E. KNECHT, Ph.D., F.I.C.,
Head of the Chemistry and Dyeing Department of the Technical School, Manchester; Editor of "The Journal of the Society of Dyers and Colourists;"

CHR. RAWSON, F.I.C., F.C.S.,
Late Head of the Chemistry and Dyeing Department of the Technical College, Bradford; Member of Council of the Society of Dyers and Colourists;

And RICHARD LOEWENTHAL, Ph.D.

GENERAL CONTENTS.—Chemical Technology of the Textile Fabrics—Water—Washing and Bleaching—Acids, Alkalies, Mordants—Natural Colouring Matters—Artificial Organic Colouring Matters—Mineral Colours—Machinery used in Dyeing—Tinctorial Properties of Colouring Matters—Analysis and Valuation of Materials used in Dyeing, &c., &c.

"This MOST VALUABLE WORK . . . will be widely appreciated."—*Chemical News.*

"This authoritative and exhaustive work . . . the MOST COMPLETE we have yet seen on the subject."—*Textile Manufacturer.*

"The MOST EXHAUSTIVE and COMPLETE WORK on the subject extant."—*Textile Recorder.*

"The distinguished authors have placed in the hands of those daily engaged in the dye-house or laboratory a work of EXTREME VALUE and UNDOUBTED UTILITY . . . appeals quickly to the technologist, colour chemist, dyer, and more particularly to the rising dyer of the present generation. A book which it is refreshing to meet with."—*American Textile Record.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

Companion-Volume to MM. Knecht and Rawson's "Dyeing."

TEXTILE PRINTING:

A PRACTICAL MANUAL.

Including the Processes Used in the Printing of

COTTON, WOOLLEN, SILK, and HALF-SILK FABRICS.

BY

C. F. SEYMOUR ROTHWELL, F.C.S.,

Mem. Soc. of Chemical Industries; late Lecturer at the Municipal Technical School, Manchester.

In Large 8vo, with Illustrations and Printed Patterns. Price 21s.

GENERAL CONTENTS.

Introduction.
The Machinery Used in Textile Printing.
Thickeners and Mordants.
The Printing of Cotton Goods.
The Steam Style.
Colours Produced Directly on the Fibre.
Dyed Styles.
Padding Style.
Resist and Discharge Styles.
The Printing of Compound Colourings, &c.
The Printing of Woollen Goods.
The Printing of Silk Goods.
Practical Recipes for Printing.
Appendix.
Useful Tables.
Patterns.

"BY FAR THE BEST and MOST PRACTICAL BOOK ON TEXTILE PRINTING which has yet been brought out, and will long remain the standard work on the subject. It is essentially practical in character."—*Textile Mercury.*

"THE MOST PRACTICAL MANUAL of TEXTILE PRINTING which has yet appeared. We have no hesitation in recommending it."—*The Textile Manufacturer.*

"UNDOUBTEDLY MR. ROTHWELL'S book is THE BEST which has appeared on TEXTILE PRINTING, and worthily forms a Companion-Volume to 'A Manual on Dyeing.'"—*The Dyer and Calico Printer.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

Large 8vo. Handsome Cloth. 12s. 6d.

BLEACHING & CALICO-PRINTING.

A Short Manual for Students and Practical Men.

BY GEORGE DUERR,

Director of the Bleaching, Dyeing, and Printing Department at the Accrington and Bacup Technical Schools; Chemist and Colourist at the Irwell Print Works.

ASSISTED BY WILLIAM TURNBULL

(of Turnbull & Stockdale, Limited).

With Illustrations and upwards of One Hundred Dyed and Printed Patterns designed specially to show various Stages of the Processes described.

GENERAL CONTENTS.—COTTON, Composition of; BLEACHING, New Processes; PRINTING, Hand-Block; Flat-Press Work; Machine Printing—MORDANTS—STYLES OF CALICO-PRINTING: The Dyed or Madder Style, Resist Padded Style, Discharge and Extract Style, Chromed or Raised Colours, Insoluble Colours, &c. — Thickeners — Natural Organic Colouring Matters —Tannin Matters — Oils, Soaps, Solvents —Organic Acids—Salts—Mineral Colours—Coal Tar Colours—Dyeing—Water, Softening of—Theory of Colours —Weights and Measures, &c.

"When a READY WAY out of a difficulty is wanted, it is IN BOOKS LIKE THIS that it is found."—*Textile Recorder.*

"MR. DUERR'S WORK will be found MOST USEFUL . . . . The information given of GREAT VALUE. . . . The Recipes THOROUGHLY PRACTICAL."—*Textile Manufacturer.*

GARMENT DYEING AND CLEANING.

A Practical Book for Practical Men.

BY GEORGE H. HURST, F.C.S.,

Member of the Society of Chemical Industry.

With Numerous Illustrations. 4s. 6d.

GENERAL CONTENTS.—Technology of the Textile Fibres—Garment Cleaning —Dyeing of Textile Fabrics—Bleaching—Finishing of Dyed and Cleaned Fabrics—Scouring and Dyeing of Skin Rugs and Mats—Cleaning and Dyeing of Feathers—Glove Cleaning and Dyeing—Straw Bleaching and Dyeing—Glossary of Drugs and Chemicals—Useful Tables.

"AN UP-TO-DATE hand book has long been wanted, and Mr. Hurst has done nothing more complete than this. An important work, the more so that several of the branches of the craft here treated upon are almost entirely without English Manuals for the guidance of workers. The price brings it within the reach of all."—*Dyer and Calico-Printer.*

"Mr. Hurst's WORK DECIDEDLY FILLS A WANT . . . ought to be in the hands of EVERY GARMENT DYER and cleaner in the Kingdom"—*Textile Mercury.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

Fifteenth Annual Issue. Handsome cloth, 7s. 6d.

THE OFFICIAL YEAR-BOOK

OF THE

SCIENTIFIC AND LEARNED SOCIETIES OF GREAT BRITAIN AND IRELAND.

COMPILED FROM OFFICIAL SOURCES.

Comprising (together with other Official Information) LISTS of the PAPERS read during 1897 before all the LEADING SOCIETIES throughout the Kingdom engaged in the following Departments of Research:—

§ 1. Science Generally: *i.e.*, Societies occupying themselves with several Branches of Science, or with Science and Literature jointly.
§ 2. Mathematics and Physics.
§ 3. Chemistry and Photography.
§ 4. Geology, Geography, and Mineralogy.
§ 5. Biology, including Microscopy and Anthropology.
§ 6. Economic Science and Statistics.
§ 7. Mechanical Science, Engineering, and Architecture.
§ 8. Naval and Military Science.
§ 9. Agriculture and Horticulture.
§ 10. Law.
§ 11. Literature.
§ 12. Psychology.
§ 13. Archæology.
§ 14. MEDICINE.

"'The Year-Book of Societies' FILLS A VERY REAL WANT."—*Engineering.*

"INDISPENSABLE to any one who may wish to keep himself abreast of the scientific work of the day."—*Edinburgh Medical Journal.*

"The YEAR-BOOK OF SOCIETIES is a Record which ought to be of the greatest use for the progress of Science."—*Lord Playfair, F.R.S., K.C.B., M.P., Past-President of the British Association.*

"It goes almost without saying that a Handbook of this subject will be in time one of the most generally useful works for the library or the desk."—*The Times.*

"British Societies are now well represented in the 'Year-Book of the Scientific and Learned Societies of Great Britain and Ireland.'"—(Art. "Societies" in New Edition of "Encyclopædia Britannica," vol. xxii.)

Copies of the FIRST ISSUE, giving an Account of the History, Organization, and Conditions of Membership of the various Societies, and forming the groundwork of the Series, may still be had, price 7/6. *Also Copies of the following Issues.*

The YEAR-BOOK OF SOCIETIES forms a complete INDEX TO THE SCIENTIFIC WORK of the year in the various Departments. It is used as a ready HANDBOOK in all our great SCIENTIFIC CENTRES, MUSEUMS, and LIBRARIES throughout the Kingdom, and has become an INDISPENSABLE BOOK OF REFERENCE to every one engaged in Scientific Work.

FOURTH EDITION, REVISED. With Additional Illustrations. Price 6s.

PRACTICAL SANITATION:

A HAND-BOOK FOR SANITARY INSPECTORS AND OTHERS INTERESTED IN SANITATION.

By GEORGE REID, M.D., D.P.H.,

Fellow, Mem. Council, and Examiner, Sanitary Institute of Great Britain, and Medical Officer to the Staffordshire County Council.

With an Appendix on Sanitary Law.

By HERBERT MANLEY, M.A., M.B., D.P.H.,

Medical Officer of Health for the County Borough of West Bromwich.

GENERAL CONTENTS.—Introduction—Water Supply: Drinking Water, Pollution of Water—Ventilation and Warming—Principles of Sewage Removal—Details of Drainage; Refuse Removal and Disposal—Sanitary and Insanitary Work and Appliances—Details of Plumbers' Work—House Construction—Infection and Disinfection—Food, Inspection of; Characteristics of Good Meat; Meat, Milk, Fish, &c., unfit for Human Food—Appendix: Sanitary Law; Model Bye-Laws, &c.

"A VERY USEFUL HANDBOOK, with a very useful Appendix. We recommend it not only to SANITARY INSPECTORS, but to HOUSEHOLDERS and ALL interested in Sanitary matters."—*Sanitary Record.*

THIRD EDITION, REVISED. *Large Crown 8vo. Handsome Cloth.* 4s.

A MANUAL OF AMBULANCE.

By J. SCOTT RIDDELL, C.M., M.B., M.A.,

Senior Asst.-Surgeon, Aberdeen Royal Infirmary; Lecturer and Examiner to the Aberdeen Ambulance Association; Examiner to the St. Andrew's Ambulance Association, Glasgow, and the St. John Ambulance Association, London.

With Numerous Illustrations and Full Page Plates.

General Contents.—Outlines of Human Anatomy and Physiology—The Triangular Bandage and its Uses—The Roller Bandage and its Uses—Fractures—Dislocations and Sprains—Hæmorrhage—Wounds—Insensibility and Fits—Asphyxia and Drowning—Suffocation—Poisoning—Burns, Frost-bite, and Sunstroke—Removal of Foreign Bodies from (*a*) The Eye; (*b*) The Ear; (*c*) The Nose; (*d*) The Throat; (*e*) The Tissues—Ambulance Transport and Stretcher Drill—The After-treatment of Ambulance Patients—Organisation and Management of Ambulance Classes—Appendix: Examination Papers on First Aid.

"A CAPITAL BOOK. . . . The directions are SHORT and CLEAR, and testify to the hand of an able surgeon."—*Edin. Med. Journal.*

"This little volume seems to us about as good as it could possibly be. . . . Contains practically every piece of information necessary to render First aid. . . . Should find its place in EVERY HOUSEHOLD LIBRARY."—*Daily Chronicle.*

"So ADMIRABLE is this work, that it is difficult to imagine how it could be better."—*Colliery Guardian.*

LONDON: CHARLES GRIFFIN & CO., LIMITED, EXETER STREET, STRAND.

"Boys COULD NOT HAVE A MORE ALLURING INTRODUCTION to scientific pursuits than these charming-looking volumes."—Letter to the Publishers from the Headmaster of one of our great Public Schools.

OPEN-AIR STUDIES IN BOTANY:

SKETCHES OF BRITISH WILD FLOWERS IN THEIR HOMES.

BY

R. LLOYD PRAEGER, B.A., M.R.I.A.

Illustrated by Drawings from Nature by S. Rosamond Praeger, and Photographs by R. Welch.

Handsome Cloth, 7s. 6d. Gilt, for Presentation, 8s. 6d.

GENERAL CONTENTS.—A Daisy-Starred Pasture—Under the Hawthorns—By the River—Along the Shingle—A Fragrant Hedgerow—A Connemara Bog—Where the Samphire grows—A Flowery Meadow—Among the Corn (a Study in Weeds)—In the Home of the Alpines—A City Rubbish-Heap—Glossary.

"A FRESH AND STIMULATING book . . . should take a high place . . . The Illustrations are drawn with much skill."—*The Times.*

"BEAUTIFULLY ILLUSTRATED. . . . One of the MOST ACCURATE as well as INTERESTING books of the kind we have seen."—*Athenæum.*

"Redolent with the scent of woodland and meadow." *The Standard.*

"A Series of STIMULATING and DELIGHTFUL Chapters on Field-Botany."—*The Scotsman.*

"A work as FRESH in many ways as the flowers themselves of which it treats. The RICH STOR of information which th book contains."—*The Garden.*

OPEN-AIR STUDIES IN GEOLOGY:

An Introduction to Geology Out-of-doors.

BY

GRENVILLE A. J. COLE, F.G.S., M.R.I.A.,

Professor of Geology in the Royal College of Science for Ireland.

With 12 Full-Page Illustrations from Photographs. Cloth. 8s. 6d.

GENERAL CONTENTS.—The Materials of the Earth—A Mountain Hollow—Down the Valley—Along the Shore—Across the Plains—Dead Volcanoes—A Granite Highland—The Annals of the Earth—The Surrey Hills—The Folds of the Mountains.

"The FASCINATING 'OPEN-AIR STUDIES' of PROF. COLE give the subject a GLOW OF ANIMATION . . . cannot fail to arouse keen interest in geology."—*Geological Magazine.*

"EMINENTLY READABLE . . . every small detail in a scene touched with a sympathetic kindly pen that remind one of the lingering brush of a Constable."—*Nature.*

"The work of Prof Cole combines ELEGANCE of STYLE with SCIENTIFIC THOROUGHNESS."—*Petermann's Mittheilungen.*

"The book is worthy of its title: from cover to cover it is STRONG with bracing freshness of the mountain and the field, while its ACCURACY and THOROUGHNESS show that it is the work of an earnest and conscientious student. . . . Full of picturesque touches which are most welcome."—*Natural Science*

"A CHARMING BOOK, beautifully illustrated."—*Athenæum.*